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Review

Year 2020: A Snapshot of the Last Progress in Flexible Printed Gas Sensors

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Abstract: A review of recent advances in flexible printed gas sensors is presented. During the last years, flexible electronics has started to offer new opportunities in terms of sensors features and their possible application fields. The advent of this technology has made sensors low-cost, thin, with a large sensing area, lightweight, wearable, flexible, and transparent. Such new characteristics have led to the development of new gas sensor devices. The paper makes some statistical remarks about the research and market of the sensors and makes a shot of the printing technologies, the flexible organic substrates, the functional materials, and the target gases related to the specific application areas. The conclusion is a short notice on perspectives in the field.

Keywords: gas sensors; flexible substrates; printed electronics; nanomaterials; wearable devices

1. Toward Flexible Gas Sensors Era

A human being collects information about the surrounding environment through its senses resulting in an emotional or intellectual behavior. In a similar way, a sensor elaborates the signals perceived by a sensing element responding with analytical data. Sensors have become an indispensable expansion of our senses and of our action opportunities by collecting information otherwise not available. The term "sensor" started to gain currency during the 1970s, identifying a transducer (or a device) that detects and converts events or changes in its environment into data directly observed or processed. The measured quantity and the provided output data can be of different nature (chemical, electrical, magnetic, mechanical, thermal, optical, etc.) making the sensors an essential tool in scientific applications, in industrial field as well as in everyday life. Over the years, the development of numerous types of sensors ranging from industrial process control to healthcare or medical diagnosis is so increased that the first decade of the 21st century has been defined as "the sensor decade" [1]. Figure 1 shows the trend of documents number related to the sensor topic available on Scopus database [2] from the year 1950. It clearly highlights the fast growth of published documents per year, from 2000 to the present day.

Nowadays, the development of sensors is certainly supported by technological improvements, in term of introduction of new nanostructured materials, new organic materials, new fabrication processes, miniaturization and the potentiality of micro- and nano-electronics and it is further enhanced by the huge market demand. Indeed, the sensors are crucial elements in "Internet of Things (IoT)". IoT is a network that collects, communicates and shares data from and between smart objects which in turn interact with the environment and people [3]. This powerful network rapidly advances, promoting the implementation of sensors in a large number of our everyday life objects, becoming them smart. In IoT framework, smart objects are coupled with radio frequency identification (RFID) smart tags, that include sensors and they are able to sense, monitor, and adapt to their environment. Intelligent

RFID tags have the aim to combine sensing, computation and communication into a single, small and versatile device [4].

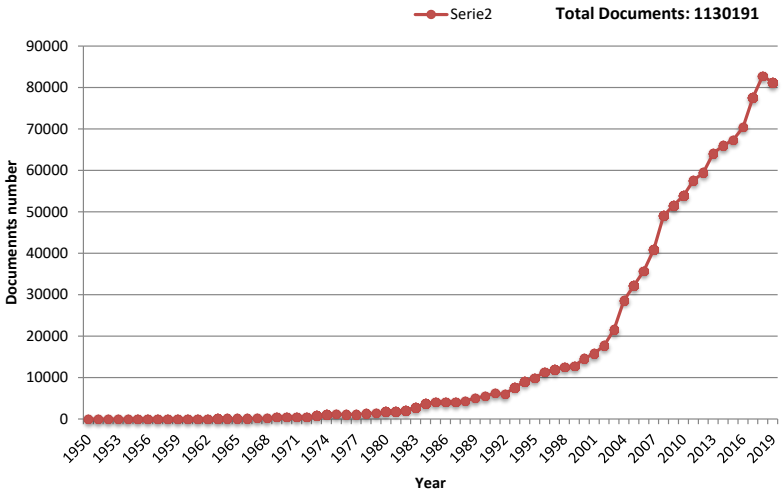

Figure 1. Number of publications per year with titles, abstract or keywords including the term "sensor" (Source: Scopus [2]).

Sensors play also a key role in development and implementation of robots, automation and control systems in the factory field. By equipping robotic devices with sensors, robotic machines have become increasingly capable of performing complex and more accurate tasks, allowing manufacturers to increase efficiency, productivity, and profitability [5].

Another promising driver of sensors need during the next years is the development of "digital twin" (digital representation of a real-world entity or system such as industrial machines, humans or cities). The digital twin is linked in near real time to its corresponding real twin equipped with suitable sensors that monitor the real counterpart and its environment. The twins are used to understand the state of the analyzed system, its response to changes and the way to improve the operation of the real system [6].

The class of gas sensors represents one of the most diffused sensors group due to the variety of structures, materials and working principles available to realize them. In addition, they present many advantages such as working in real time, to be easy implemented and managed, to have long lifetime and low cost [7]. For these reasons, they are suitable to be used in many fields of applications, mainly related to the human health and security, as for instance:

- Air quality monitoring (indoor and outdoor) [8,9];
- Vehicle emission monitoring [10,11];
- Alarming of leakage of toxic and hazardous gases [12];
- Personal healthcare [13];
- Medical diagnosis [14];
- Food quality monitoring [15,16],
- Agricultural and farming emission monitoring [4,17].

Figure 2 shows the trend of publications number focused on gas sensors obtained by using Scopus database [2]. In 1815, Davy developed the first indispensable gas detector (Davy's lamp) for coalminers against methane [18]; in 1926, Johnson produced the first commercial catalytic combustion gas detector [19]. Afterwards, only few papers can be found until 1970. The first significant studies related to the development of gas sensors started at the beginning of the seventies, they rapidly increased since 2002 reaching today more than two-thousand documents per year.

In the same way, also the gas sensor market is continuously increasing. Recent published reports stated that the gas sensor global market isn't just growing, but it is accelerating. Indeed, it is

expected to grow at a Compound Annual Growth Rate (CAGR) of approximately 7% during the period 2017–2023 [20] until reaching 3 billion dollars in 2027 [21].

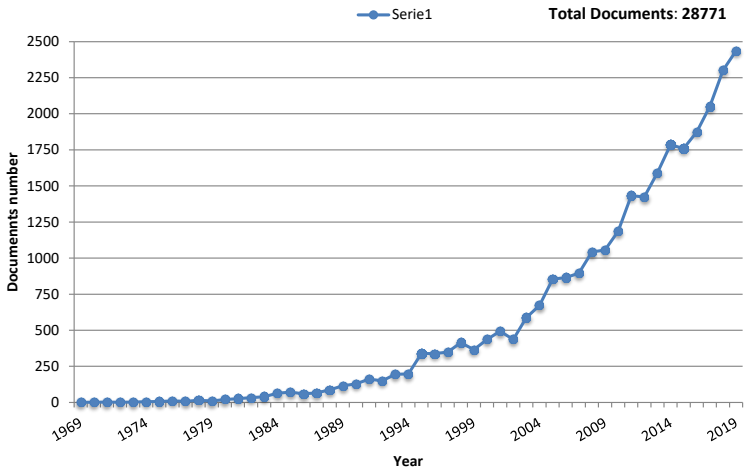

Figure 2. Number of publications per year with titles, abstract or keywords including the terms "gas sensor" (Source: Scopus [2]).

A gas sensor is a complex system consisting of different elements (generally a sensing element, a substrate, electronics and case) chosen according to the final application and each one responsible for the good operation of the device. With this in mind, the suitable sensing mechanism, the appropriate substrate and the most convenient and compatible fabrication method have to be selected. Figure 3 summarizes some sensing mechanisms, substrates and fabrication methods, typically used.

The most common sensing mechanisms are based on:

- A non-Nernstian potential is caused at each electrode/electrolyte/gas interface by differences in the redox kinetics of various gases (mixed-potential sensors among the electrochemical sensors) [22,23];
- A variation of sensing layer conductance proportional to the concentration of the target gas (chemiresistive gas sensors) [24];
- A variation of the capacitance of the sensing element proportionally to the concentration of the target gas when an optimized signal frequency is applied (capacitive gas sensors) [25];
- A variation of the source-drain current as a function of the concentration of the target gas (field-effect transistor-based gas sensors) [26];
- A variation in terms of amplitude or frequency of a wave propagating on the surface of the sensing layer due to the presence of the target gas (mechanical gas sensors) [27]; the measurement of the optical absorption at specific wavelengths depending on each gas (optical gas sensors) [28,29].

To produce gas sensors, many fabrication methods are available, among them self-assembly [30], chemical vapor deposition (CVD) [31], physical vapor deposition (FVD) [32], micromachining [33], printing [34], and coating [35]. In some cases, the same methods are used to develop also sensor electronics, for example by means of printing [36].

Substrates can be subdivided in two main classes: traditional rigid substrates such as silicon, silicon carbide or ceramics (Al_2O_3, ZrO_2) [37] and recent flexible substrates, generally based on organic materials (paper, polymers and textiles) [38,39].

Flexible substrates have immediately attracted the attention of research and industry due to their suitability to be used in wearable and flexible electronic devices, in RFID smart tags, and in general to be easily implemented in smart objects meeting the IoT requirements. Flexible substrates have been also used in the area of gas sensors, because they have been found to offer more opportunities in terms of new possible applications. Simultaneously, the number of researches devoted to substrate

characterizations and its coupling with the sensing element has grown, leading to the development of new functional materials and to optimization of the fabrication techniques.

Figure 4 shows the trend of publications targeting flexible electronics and flexible gas sensors obtained through Scopus database [2], both increased in the last 20 years.

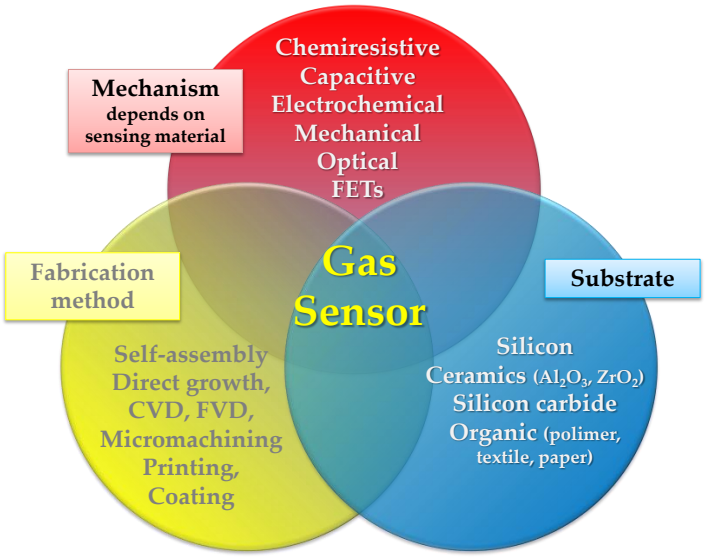

Figure 3. Scheme of the most used sensing mechanisms, substrates and fabrication methods to develop a gas sensor.

This review paper concerns flexible printed chemiresistive gas sensors, currently the more attractive choice, because they combine the large variety of functional materials, suitable to detect a wide range of gases down to ppb level, with printing techniques that allow large-scale production at low cost. A description of the main printing technologies, flexible organic substrates, functional materials, and target gases related to the specific application areas is reported in the following sections, concluding with a short notice on achievements and perspectives in the field.

Table 1 represents a shot of the current state of art about flexible printed chemiresistive gas sensors, in which room temperature (RT) is referred to a working temperature between 20 and 25 °C.

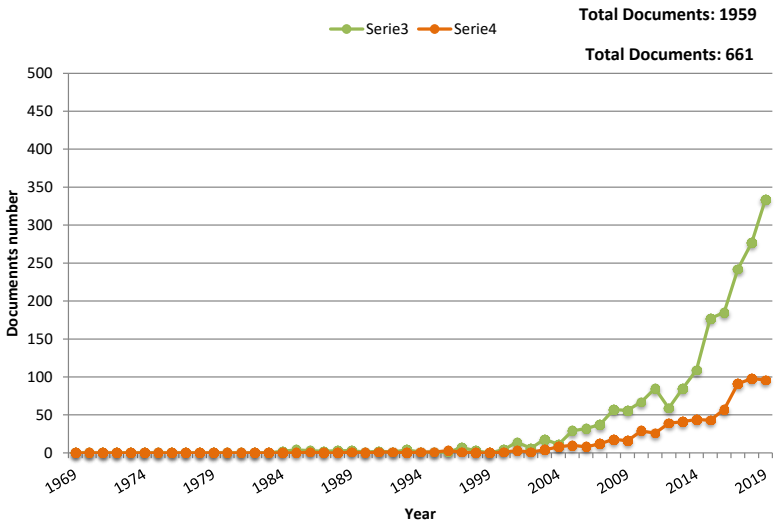

Figure 4. Number of publications per year with titles, abstract or keywords including the terms "flexible electronics" and "flexible gas sensor" (Source: Scopus [2]).

Table 1. Shot of the current state of art about flexible printed chemiresistive gas sensors.

Printing Technique	Substrate Material [1]	Functional Material [1]	Gas Detected [2]	Working Condition	Gas Concentration	Year, Ref.
Inkjet printing	PET	PANI	NH_3	RT	100 ppm	2008 [40]
Inkjet printing	PET	rGO	NH_3 NO_2	RT	100 ppm 10 ppm	2010 [41]
Inkjet printing	Photo paper	PEDOT/PSS	NH_3	RT	100 ppm	2012 [42]
Inkjet printing	Cellulosic paper	CNT	NO_2 Cl_2	RT	100 ppm 20 ppm	2012 [43]
Inkjet printing	Paper with barrier layes	CuAc	H_2S	RT	10 ppm	2012 [44]
Inkjet printing	Kaolin-coated paper	PANI-$CuCl_2$	H_2S	RT dry/wet	15 ppm	2013 [45]
Inkjet printing	PEN	(PVC/Cumene-PSMA/PSE/PVP)—CNTs	NH_3	RT	100 ppm	2014 [46]
Inkjet printing	Plastic substrate	Graphene, PEDOT/PSS, PEDOT/PSS- graphene	NH_3	RT	500 ppm	2014 [47]
Inkjet printing	PI	SnO_2	NO_2 CO	300 °C	20 ppm 20 ppm	2016 [48]
Inkjet printing	Textile	PANI	NH_3	RT	15–100 ppm	2016 [49]
Inkjet printing	PET	rGO-Ag	NH_3	RT	15 ppm	2017 [50]
Inkjet printing	PI	Pd-SnO_2	CO NO_2	250 °C dry/25%RH	20, 35, 50 ppm 1, 3, 5 ppm	2019 [51]
Inkjet printing	PI	PEDOT:PSS with $FeCl_3$ additives	NH_3	RT	0.1–200 ppm	2019 [52]
Inject printing	PET	CuO	H_2O C_2H_5OH Methanol	RT	45–100% RH	2019 [53]
Inkjet printing	Flexible, transparent	PEDOT:PSS/MWCNTs-N_2	CH_2O	RT	10–200 ppm	2019 [54]
Inkjet printing	PI	SnO_2	C_2H_5OH NH_3 CO	300 °C	dry and wet air	2019 [55]
Plasma jet printing	Paper	MWCNTs	NH_3	RT	60 ppm	2016 [56]
Screen printing	PET	TiO_2	H_2O	RT	5–70% RH	2017 [57]
Screen printing	Flexible substrate	SnO_2	C_2H_5OH 2propanol C_6H_3O	RT 30% RH	1–500 ppm 1–500 ppm 1–500 ppm	2019 [58]
Gravure printing	PI	Ag-S-rGO	NO_2	RT	500 ppb	2014 [59]
Gravure printing	PET	PEDOT/PSS PANI	H_2O NH_3	RT	40% RH 100 ppm	2015 [60]
Gravure printing	PI	WO_3-PEDOT/PSS	NO_2	RT	5 ppb	2015 [61]
Gravure printing	HDPE	PANI-ITO	NH_3	RT 50% RH	1–100 ppm	2019 [62]
Nanoimprint lithography	Polycarbonate	Pd	H_2	RT	3500 ppm	2013 [63]
Printing	Polymer	-	C_6H_3O	-	-	2019 [64]

[1] PET, polyethylene terephthalate; PEN, polyethylene naphthalate; PI, polyimide; CNT carbon nanotubes; MWCNT, multi-walled carbon nanotubes; GO, graphene oxide; rGO, reduced graphene oxide; PANI, polyaniline; PEDOT, poly(3,4-ethylenedioxythiophene); PSS, polystyrene sulfonated acid; PVP, polyvinylpyrrolidone; PSS, poly(4-styrenesulfonic acid) sodium salt; PPV, polypyr-role; PVC, polyvinyl chloride; Cumene-PSMA, cumene terminated polystyrene-co-maleic anhydride; PSE, poly(styrene-co-maleic acid) partial isobutyl/methyl mixed ester; CuAc, copper acetate. [2] Gases are described in the Section 5.

2. Printing Techniques

Printing is the most used technique to produce flexible electronics and flexible sensors due to its great number of advantages. It is a bottom-up process, where layers are added one by one: both electrodes and also different functional materials can be deposited with the same technique even on the same substrate. The intrinsic decoupling between the ink preparation (starting from the synthesis of functional material) and the film deposition allow the optimization of the whole procedure in terms of simplification, wastage and costs reduction. Printing permits the large-scale fabrication with low cost production. The use of this technique on a flexible organic substrate makes possible the deposition of a pattern/layer also on non-planar surfaces and on areas larger than that the conventional rigid substrates and at temperatures suitable for organic materials. The number of fabrication steps in printing techniques is lower than that for standard microfabrication technology. It could be performed in ambient condition by using ecofriendly and not hazardous starting materials [65,66].

Printing techniques can be grouped in two main classes depending on the presence of a physical contact or non-contact between the ink and the substrate during deposition. In the first class can be included gravure printing, nano-imprinting, flexographic printing, and transfer printing, while screen printing, inkjet printing, etc. are belong to non-contact method. Detailed description of all these processes is given in a comprehensive review [65], while a summary of the more advantageous single techniques to prepare chemiresistive gas sensors is reported below [67].

Nano-imprinting—Involves different steps and allows to have printed layers with thickness among 1 and 20 µm. A rigid substrate lodges a continuous layer that is subsequently patterned pressing with a mold. The patterned layer is demolded, thermally treated, and then transferred on the flexible substrate [65]. Until now, only one chemiresistive flexible gas sensor was prepared by nanoimprinting. It is a palladium film which was transferred into a polycarbonate film to reveal hydrogen [63].

Gravure printing—A simplest gravure printer is composed by a rotating printing cylinder with the printing pattern incised on its surface. The ink is released using a nozzle on the top of the cylinder while a doctor blade removes the ink excess before the deposition on the moving substrate. The printed film quality depends on the pattern and on the ink viscosity. This method allows printing speeds in the range of 8–100 m/min, greater than that of the here considered techniques [65]. As shown in the Table 1 few chemiresistive flexible gas sensors are fabricated by gravure printing [59–62].

Screen printing—Is the most used technique to fabricate thick film chemiresistive gas sensors on ceramic (such as alumina) substrate [65–68]. In the case of flexible chemoresistive gas sensors, inkjet printing is preferred in terms of R2R implementation, reliability and no waste production. However, screen printing is still widely used for electrodes fabrication.

The fundamental tool is the screen that is made of a mesh (e.g., polymer or aluminum threads) mounted on a frame under tension. Finer and smaller openings of the mesh are needed to print a pattern with higher degree of detail. The screen is placed above a substrate. Ink, located on top of the screen, is pressed by a squeegee through the holes of the mesh. The ink is deposited on the substrate in a controlled amount, proportional to the thickness of the mesh. The thickness of the printed layer ranges from 5 to 30 µm. As the squeegee moves toward the rear of the screen the tension of the mesh pulls the mesh up away from the substrate (named snap-off), leaving the ink upon the substrate surface. An example of TiO_2 based flexible gas sensor made by using screen printing on PET substrate is reported in the reference [57]. Screen printing can be used also changing the screen with a stencil to prepare electrodes [69] or sensing layer. The printing pattern corresponds to the openings of the stencil. The printing process needs a squeegee that spreads the ink with a proper viscosity.

Inkjet printing—Is the most used technique to manufacture chemiresistive printed flexible gas sensors (see Table 1). There are many examples of flexible gas sensors, highlighting the possibility to print organic, inorganic and their composites functional materials-based inks. Inks are solutes dissolved or dispersed in a solvent. They are ejected in a proper amount through a nozzle activated by a thermal, piezoelectric or electro-hydrodynamic control that allows the 'drop-on-demand' (DOD) printing mode. Apart from the evaporation of the solvent, the thickness of the deposited layer (ranging

from 0.01 and 0.5 µm) is dependent on the viscosity of the ink [65]. Beside its large use, inkjet-printing has some limitation: in fact, the need to have only inks in a liquid phase could be not immediate for all the different functional materials. Furthermore, this printer works at a relatively high operating temperature (200–300 °C) [48].

Recent advances in printing techniques and in new materials preparation, together with the growing sensors market demand, have led to the development of fast and efficient avenues for sensors mass production.

Roll-to-roll printing (R2R)— Represents the solution: it is a continuous line production in which a series of different printing and curing/sintering systems can be implemented to achieve the deposition of various materials on a same flexible and large substrate roll. The coupling of the single techniques represents a crucial task, because many parameters and boundary conditions have to be assessed concerning the materials/inks properties and treatments and the synchronization of the substrate motion during the complete deposition. All the four described single printers could be implemented in an R2R line [65].

Figure 5 shows pictures representative of the above described printing technologies (gravure printing, nano-imprinting, screen printing, inkjet printing and R2R).

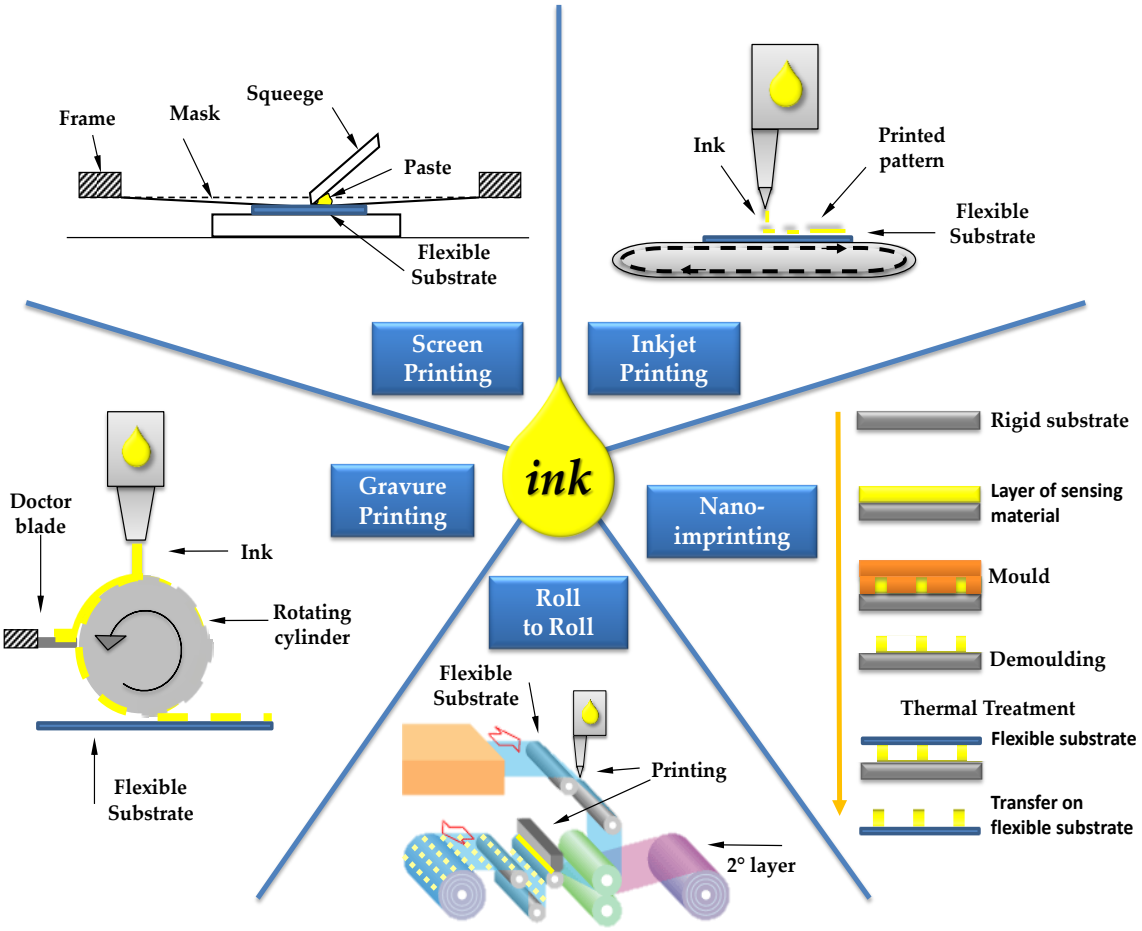

Figure 5. Scheme of the most used printing techniques to prepare chemiresistive gas sensors on flexible substrates.

3. Flexible Substrates

Thin glass, metal foils and plastics could be used to fabricate flexible electronics [70,71]. However, only plastic foils permit a low cost, high-speed production over large areas by using various printing technologies in an R2R production line. Thin glass has an intrinsic fragile nature that limits its flexibility,

while metal foils have good resistance to high temperatures, but are inadequate due to their surface roughness and high cost. Furthermore, recent advances have involved paper and textile as flexible substrates to lodge electronics and sensor devices. Until now, printed flexible chemiresistive gas sensors were prepared using plastic, paper and textile substrates.

Plastic substrates—In general, the polymer substrates should mimic the properties of planar rigid substrates. Dimensional and thermal stability, low coefficient of thermal expansion, good solvent resistance and good barrier properties for moisture, air and gases are necessary for plastic substrates [69–72]. In addition to physical, chemical, mechanical and optical performances, also the glass transition temperatures of different polymers have to be evaluated depending on the final application and the fabrication process involved. In a previous review [65] characteristic properties of most used polymers in flexible electronics were reported.

To fabricate flexible gas sensors, polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polyimide (PI), polycarbonate are mainly chosen [73–75]. They are characterized by glass transition temperatures lower than 300 °C. Thermal treatments in fabrication steps could induce a substrate expansion damaging the device. Humidity affects the plastic resistivity, water absorption increases the substrate weight and alters the dielectric constant. To bypass this problem, a thin coating made of transparent oxides is applied on its surface acting as a barrier mainly for sensors used in food and medical packaging [65].

Paper substrates—Paper could be used as a flexible substrate with numerous advantages. It is easily accessible, eco-friendly, recyclable, light, thin, with low thermal expansion coefficient, roll to roll compatible and low cost. Its main drawbacks are the surface roughness and great absorption capacity. Paper substrates are usually coated with several materials such as kaolin, and polymers [76]. Different gas sensors printed on paper substrates were fabricated through inkjet printing by using both polymer and inorganic functional materials.

Textiles—The first and most simple method to implement a flexible gas sensor on a textile is the sensor fabrication by using a polymer substrate after weaving on the textile. In [77] this method was applied using a cotton textile. Flexible printed gas sensors could be developed also by using textile as substrate. In the case reported in reference [49], textile (polypropylene (PP) spun-bonded non-woven) is the substrate on which the sensing layer was deposited. In other studies, through the functionalization of nylon or cotton-based yarns, sensitive textiles were obtained [78,79]. However, in this configuration the yarn could be stressed during the weaving process.

Regarding the influence of the substrate materials on the gas sensor performances, a useful comparative study has been carried out by Khan et al. in [80]. They prepared VOCs sensors through inkjet printing depositing a carbon black paste as functional material on PET (polyethylene terephthalate), paper and cotton fabric substrates. About the ink printability, the authors observed that the sensing material impregnates the paper and the cotton fabric substrates merging ink and substrate into one. This is an ideal feature when the sensors have to be bended or mounted on planar structures. Furthermore, sensors on cotton and paper substrates exhibited better sensing performances with respect to sensors printed on PET substrates. In particular, the latter showed higher sensitivity but also higher responses and recovery times making those not suitable for real time applications.

4. Functional Materials

For obtaining printed gas sensors, it is necessary to prepare an ink by adding to the functional material, in form of powder, an organic vehicle consisting of a mixture of rheological agents in volatile solvents. The amount and composition of the organic media make the ink printable and give to the films some electrical properties and the macroscopic appearance. The organic vehicle is a sacrificial ingredient of the ink that completely disappears during the thermal processes carried out onto the films. The composition of the organic vehicle is determined by the requested rheological properties of the ink suitable for the specific printing technique. Generally, the proper ink viscosity for printing on

flexible substrates ranges from cP to few tens of P. Both the organic vehicle composition and the film temperature process are depending on the material substrates [65].

The sensing materials employed in the development of chemiresistive gas sensors (using a rigid or flexible substrate) are inorganic, organic and organic-inorganic composites. The detection mechanism in chemiresistive gas sensors is based on the variation of the electrical conductance as a result of surface chemical reactions with environmental gases. Among the inorganic materials, there are metals, metals oxides, carbon nanotubes, graphene and graphene oxide. The conductive polymers constitute the group of organic materials and the organic-inorganic composites are obtained by mixing inorganic and organic materials with the aim to improve the gas sensing performance of the device. Hereinafter, the above listed functional materials are discussed and examples of some flexible printed chemiresistive gas sensors are reported for each type of sensing material.

Noble metals (gold, platinum, palladium, silver, rhodium, etc.)—Are well known because they are incorporated in metal oxides, in carbon nanotubes, in graphene and graphene oxide to enhance their gas sensing properties in terms of sensibility, selectivity, response and recovery times and for lowering the working temperature. Among the noble metals, only palladium could be individually used to prepare gas sensors because it offers good performance towards hydrogen. At the same time, it is singly used to prepare flexible printed hydrogen gas sensors [63] and as doped agent of SnO_2 [51].

Metal oxides—Among the great variety of materials which can be used to prepare a device able to detect a gaseous compound with optimal characteristics of sensitivity, selectivity and electrical stability, certainly the metal oxides have shown the desired properties for using them in real working conditions. They belong to the class of wide-gap semiconductor oxides which have become of widespread interest in gas sensing due to their peculiarity of modifying surface properties when interacting with reducing or oxidizing gases. Most of them are semiconductors of type *n*, such as SnO_2, TiO_2, In_2O_3, WO_3, ZnO, Fe_2O_3, CuO, etc., and solid solutions of them, while noble metals or foreign ions are added as catalysts or conductivity modifiers, the working temperature ranging between 200 and 500 °C. Few are of *p* type, like NiO or $LaFeO_3$.

A case in point is tin dioxide, the most widely used material for gas sensing. Indeed, it is able to sense a great variety of gases, both reducing and oxidizing. On the other hand, it fails in selectivity, reason why a lot of efforts have been addressed to improve the sensing and selectivity properties modifying the material with the addition in particular of noble metals (Pd, Pt, Au) enhancing the sensitivity toward different gases, specifically methane, carbon monoxide and benzene. For all gas sensors based on metal oxides, it is of paramount importance the grain size reduction, which, leading to an enhancement in the surface-volume ratio, has opened the way to further improvements toward the sub-ppm gas detection. On this subject, a case of study has been a solid solution SnO_2-TiO_2 mixed oxide (as $Ti_xSn_{1-x}O_2$, $0 \leq x \leq 1$). It resulted that the material with Ti molar ratio of 0.3 was the best material to detect carbon monoxide at concentrations low down to about 200 ppb. This result has been due to extreme low crystallite size of 5.5 nm at the temperature of firing of 650 °C [81,82]. For the other cited materials, ZnO, synthesized in different nanoforms (see Figure 6) has shown great ability to detect acetone at sup ppm level [83], WO_3, also as solid solution $(W,Sn)O_3$ to detect NO_2 [84], TiO_2 as detector of VOCs for medical diagnosis [85].

The semiconductor oxides exhibit conductivity due to stoichiometric defects: in the ones of type *n*, such defects are oxygen vacancies behaving as donor levels; indeed, remaining the electrons weakly bounded, they easily enter into the conduction band. Such electrons contribute to the building of the Schottky barrier eVs when they are captured by the acceptor surface states (in sensing materials oxygen atoms). In nanocrystalline semiconductors, the mechanism of conduction is thereby controlled by the presence of a huge series of intergranular point contacts at which a surface barrier develops, due to the presence of charged surface states. Conductance therefore is an activated process, since only those electrons with sufficient energy to cross the barrier take part to electrical conductance. The sensing mechanism is based on the variation of the potential barrier height as a result of surface chemical reactions with environmental gases, leading to the electrical conductance modification. Such

a mechanism properly works when the temperature, usually between 200 and 500 °C, is optimized with respect to both functional material and detecting gas.

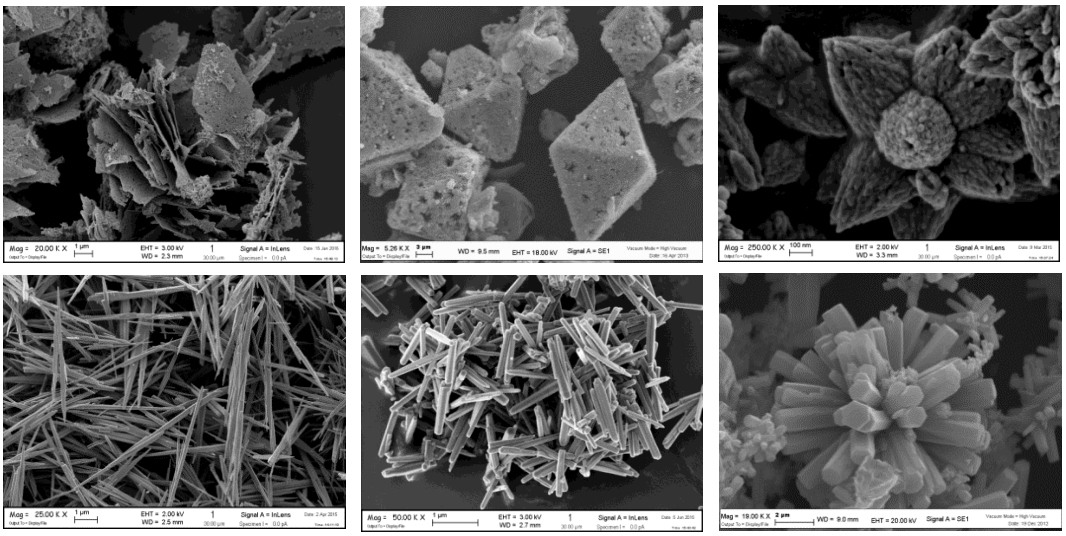

Figure 6. ZnO nanoforms tested toward acetone for breath gas analysis [83].

The metal oxides have been widely investigated also as flexible electronics. It must be highlighted that these devices can undergo thermal treatment not higher than 300 °C. Nevertheless, in the literature many publications on metal oxide gas sensors printed on flexible substrates are reported. As example, in [48] a tin dioxide sensor was developed onto polyimide foil performing electrical measurements toward carbon monoxide and nitrogen dioxide heating the device at temperatures between 200 and 300 °C. Moreover, an example of humidity sensor that works at RT is reported in [57]. TiO_2 nanoparticles were deposited by screen printing on a PET substrate with gold electrodes, obtaining the series of sensors showed in Figure 7.

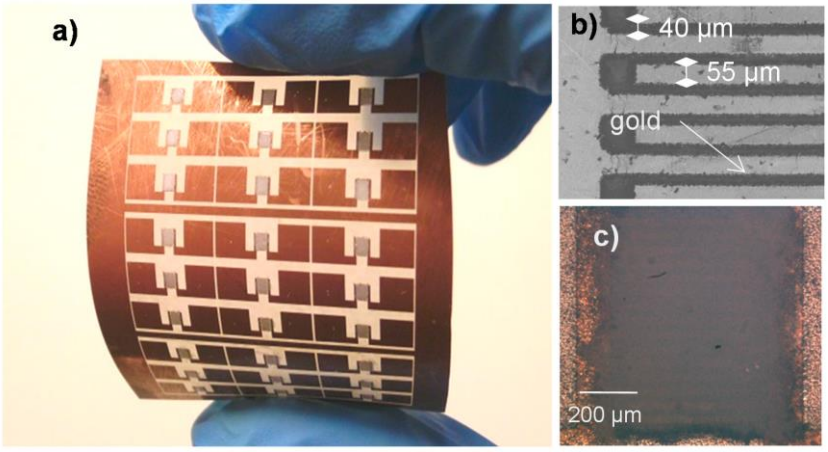

Figure 7. (**a**) Picture of 3 × 3 sensor matrices fabricated on PET substrate; (**b**) SEM image of the interdigitated electrodes; (**c**) optical image of the humidity sensors. [57].

In Figure 8,the sensors response to humidity levels varying from 0% to 70% (a), its calibration curve (b) and the response and recovery times (c) are reported. The prepared humidity sensor is able to detect the target gas down to low levels. The response and the recovery times are fast in a range of RH between 5% and 40%. This is attributable to the TiO_2 sensing mechanism toward humidity.

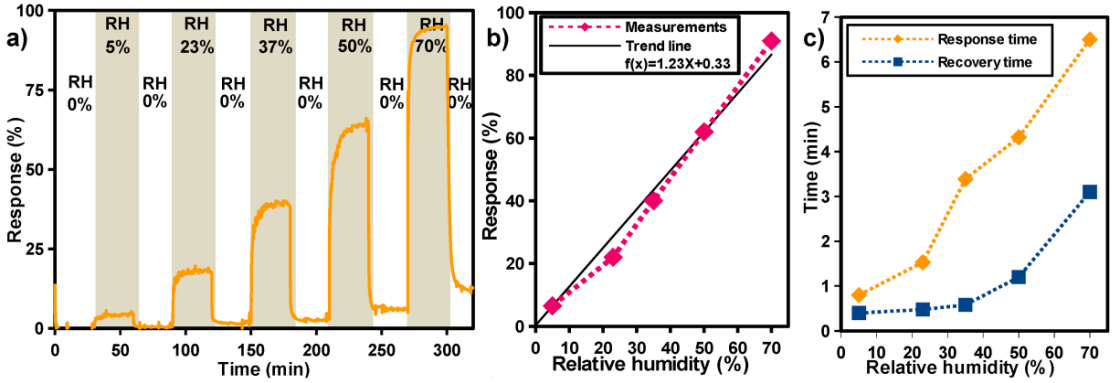

Figure 8. (**a**) response curve of the sensor to gradually increased humidity levels, ranging from 0 up to 72%; (**b**) sensor response as function of the relative humidity; (**c**) response and recovery time of the sensor as function of the relative humidity. [57].

Carbon nanotubes—Carbon nanotubes were discovered by Ijimain in 1991. They can be prepared as single (SWCNT) or multi-walled carbon nanotubes (MWCNT) and are consisting of single or several layers of graphene sheets [86]. The unique geometry, morphology, and material properties attracted the attention of many researchers. In gas sensing, it is extremely interesting the enormous surface-to-volume ratio and the hollow structure, particularly suitable for the adsorption of gas molecules. The CNTs can be prepared as gas sensors using many different technologies. Thereby, also the sensing mechanisms can be different and the variation of the CNTs properties can be detected through various methods. In [87], a comprehensive survey of current CNTs-based gas sensing technology is presented. The literature reports also various gas sensing application in flexible form. As an example, in [88] the fabrication of an inkjet printed CNT based sensor for DMMP (dimethyl methylphosphonate) detection is reported. It was achieved a sensitivity of 20% on 10 ppm of DMMP vapor.

In [89] a flexible and reliable chemiresistor-type NO_2 gas sensor based on single-walled carbon nanotubes (SWNTs) on polytetrafluoroethylene (PTFE) membrane filter substrate is described. In [36] fully printed CNT network gas sensors on flexible substrates such as polyimide (PI) and polyethylene terephthalate (PET) have been used for ammonia and nitrogen dioxide detection in air at low ppm concentrations.

Graphene and graphene oxide—Graphene is a two-dimensional crystalline material with excellent properties like large specific surface area, high conductivity, and high Young's modulus [90]. The main characteristic is that all atoms of a graphene layer can be considered as surface atoms, so being all able of adsorbing gas molecules; in such a way a very large surface area is available for the sensing mechanism. Moreover, the interaction between graphene layers and the adsorbates molecules can be of different intensity, being of van der Waals type or covalent bonding. It is also characterized by an extremely small change in the resistance due to very small concentration of gas adsorption achieving gas detection down to the molecule level. A more interesting material is graphene oxide (GO) resulting of chemical exfoliation and oxidizing of layered crystalline graphite (natural or artificial). In specific conditions of graphite oxidizing, the resulted GO maintains 2D structure, in which layers of carbon atoms are covered by oxygen-containing functional groups. GO can be obtained also by chemical synthesis in form of single layer or multilayer structure. Starting from GO, by a reduction processes (thermal, chemical, etc.) it can be obtained the reduced graphene oxide (rGO). The rGO generally contains defects due to its synthesis process. GO and rGO properties are extremely different from those of graphene, making both of them interesting for gas and chemical sensing applications. As example, the oxygenated functional groups confer hydrophilic nature to GO, highly sensitive to water molecules and therefore employed to prepare humidity sensors. The oxygenated functional groups also offer different possibilities for the surface functionalization with noble metals, metal oxides and conductive

polymers [91]. An example of flexible ammonia sensor based on rGO and nano-Ag ink deposited through inkjet printing to a PET substrate is reported in [50] and shown in Figure 9.

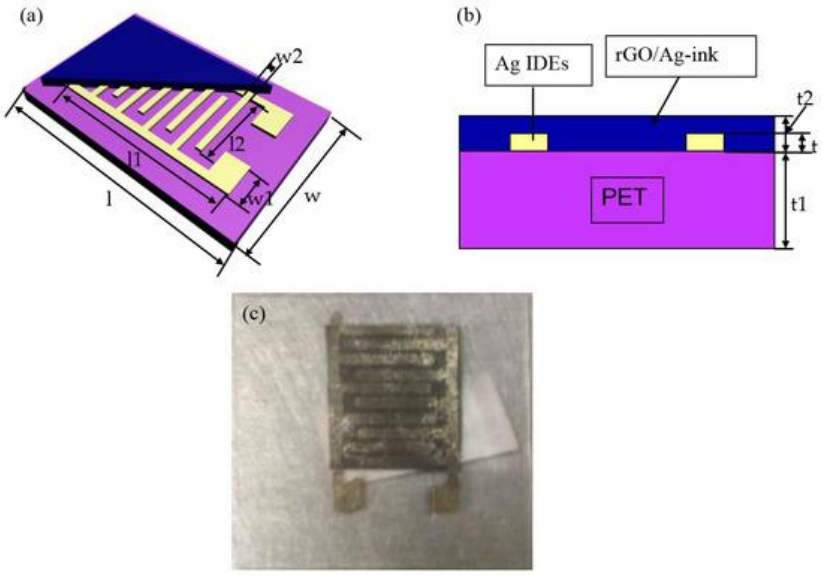

Figure 9. Schematic and physical map of the coated interdigital electrodes (IDEs) with reduced graphene oxide (rGO)/nano-silver ink (Ag-ink). (**a**) Schematic diagram; (**b**) cross-sectional view; (**c**) microscopic picture of the coated IDEs. [50].

The sensor was tested to 15 ppm, 50 ppm, 100 ppm, and 200 ppm of NH_3 at room temperature showing responses of 4.25%, 6.1%, 10.08%, and 14.7%, respectively (see Figure 10).

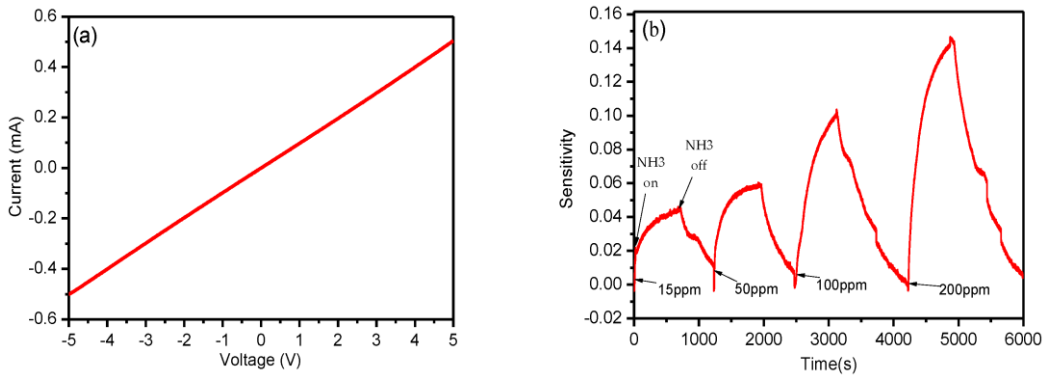

Figure 10. (**a**) Current–voltage (I-V) curves for the coated IDEs with rGO/Ag-ink; (**b**) dynamic response of the IDEs sensors to different concentrations of NH_3 at room temperature. [50].

Conducting polymers—Are easily synthetized by chemical and electrochemical processes with very low cost. From 1977, when it was found that polyacetylene became a conductive material through a suitable doping process, they have been used as functional material for gas sensing [92]. Due to the increase of the charge carriers (polarons), the polymer conductivity grows and makes it a good functional material for gas sensing at room temperature. In a conducting polymer based chemoresistive gas sensor, a change of the target gas concentration results in a polymer conductivity variation. The most used conducting polymers, also in flexible printed gas sensor development [82,83], are polyaniline, polypyrrole, poly(3,4-ethylenedioxythiophene) (PEDOT), and PEDOT doped with polystyrene sulfonated acid (PEDOT/PSS) [40,49,52]. In [92] the characteristic of printing conducting polymers to chemical sensor is described in detail. They have good sensing properties at room temperature and with high flexibility create a synergetic coupling with flexible substrates.

Organic-inorganic composites—Gas sensors based on functionalized polymers with other materials (CNTs, graphene, GO, metals or metal oxides) generally show enhanced sensing properties (in terms of sensibility, selectivity, response and recovery times) compared to those of a single polymer. As an example, in the work described in Ref. [47] a pure graphene PEDOT:PSS and a graphene-PEDOT:PSS gas sensor were prepared. The sensibilities of the sensors towards 500 ppm of NH_3 are evaluated to be 2.4%, 4.4%, and 9.6% respectively. Additionally, the composites, which are based on a polymeric matrix, exhibit a good coupling with the flexible substrates and result suitable to be printed.

5. Target Gases

In this section the most relevant gases in the areas of pollution monitoring, health issue and industries are listed and described. The continuous control of gas levels is necessary to reduce environmental pollution, to maintain safe working conditions, to prevent health disorders and to decrease industrial equipment failures. For each gas described below, there are various sensors studied and used for different applications. As examples, some of these sensors are quoted in the gas references.

Hydrogen (H_2)—Is colorless, odorless and tasteless gas, highly flammable. It forms explosive mixtures with air. The most abundant element in the universe, otherwise it is quite rare in the Earth atmosphere. It is mostly a man-made product that is used as a reagent in chemical industry, as fuel, as a power generator, or as cooler in power plants. It is a marker in human breath related to metabolic diseases (e.g., lactose intolerance or malabsorption) [93–95].

Oxygen (O_2)—Is the main gas necessary for the life and it is one of the three major constituents of Earth's atmosphere together with nitrogen and argon, and it is present at about 21% vol. In closed spaces, O_2 can decrease in concentration becoming seriously dangerous for the health. It is used in the treatments of medical diseases, in chemical and combustion processes and in automotive field, where suitably mixed to fuel allows best performances and reduces the fuel consumption [96].

Ozone (O_3)—Is an atmospheric gas with a pungent characteristic odor, irritant and poisoning for human subjects. In the ozonosphere, it is in high concentrations and it filters the sun's ultra violet rays which are otherwise dangerous for living beings. In the lower atmosphere, it is an air pollutant that causes lung dysfunctions and worsens respiratory diseases [97,98]. As chlorine, it is used in water treatment and purification.

Water vapor (H_2O)—Is the Earth's primary greenhouse gas trapping more heat than carbon dioxide. The measurement and control of water vapor is important in many areas, such as meteorology, medicine, industry and agriculture [99]. Absolute humidity (AH) is the measure in g/m^3 of water vapor in the air not dependent of temperature, while the relative humidity (RH) is the ratio of moisture in the air to the saturation level of moisture (at same temperature and pressure). Generally, the developed humidity sensors are calibrated to measure RH [100–102], thereby the absolute humidity can be measured from RH and the ambient temperature. On the other hand, H_2O is also crucial, being an interfering gas with respect to the most gases to be detected, pollutant or not. In this case, absolute humidity rather than relative humidity is the crucial parameter that determines the effects of humidity on the sensor's response [103].

Carbon monoxide (CO)—Is an odorless, colorless and flammable gas created when the combustion of hydrocarbon fuels or in a forest fire takes place in shortage of oxygen or with an insufficient temperature. Due to the fact that its affinity to hemoglobin is higher than that of oxygen, when CO level in the environment is higher than 35 ppm, it binds with hemoglobin obstructing the O_2 transportation in the body of animals and human beings. The consequences are hypoxia, body tissue damaging, cardiovascular diseases until to death [104].

Carbon dioxide (CO_2)—Is an odorless and colorless gas. It is used as reagent for the photosynthesis by plants to synthesize oxygen and glucose and it is produced during the respiration process in humans and animals. It is also produced during the combustion processes. It acts as atmospheric pollutant and it is known as the major gas responsible for the greenhouse effect. When its concentration increases can cause suffocation and if it reaches levels above 3% [104] becomes lethal.

Nitric oxide (NO)—Is a colorless, toxic, irritant and corrosive gas. It is an unavoidable by-product of fossil fuel combustion in presence of air and it is one of the primary air pollutants. It is used in the semiconductor industry and as vasodilator in medical treatments. It is a biomarker in human breath related to lung inflammation when the concentration is above 50 ppb [105].

Nitrogen dioxide (NO_2)—Is a reddish-brown gas above 21.2 °C with a pungent, acrid odor. NO_2 is produced in combustion processes of fossil fuels and in the oxidation of nitrogen. It is present in heavy traffic areas, while indoors it is produced by heaters. It is a pollutant that contributes to acid rains, and it results toxic at low levels with a threshold contact level of 1 ppm. Its exposure causes respiratory diseases until possible death. [106,107].

Ammonia (NH_3)—Is an irritant, corrosive, flammable colorless gas, with a strong pungent odor. It is used in fertilizers for intensive agriculture, in hygienic products, in textile production, as refrigerant gas and in explosives [108,109]. When its concentration exceeds the natural background that is down to few ppb, it could cause atmospheric, soil and water pollution, and severe damage for human health. In exhaled human breath, it is related to the liver failure [110] or disturbed urea balance (kidney disorder) [111], in both cases in concentration of few hundred of ppb.

Hydrogen sulphide (H_2S)—Is a colorless, flammable and corrosive gas with characteristic odor, resulting toxic even in low concentrations. It derives from volcanic activities, from decomposition of organic compounds and from the combustion of fossil fuel. Hydrogen sulfide is also the by-product of some industrial activities such as the food industry, water purification from sludge, coke production, leather tanning and oil refining [112]. The medical effects of H_2S depend on its concentration and the duration of exposure: from 10 to 500 ppm can cause various respiratory diseases and temporary or permanent damages in the nervous, cardiovascular, renal, hepatic, and hematological systems, while in concentrations over the 500–1000 ppm H_2S is immediately fatal [113].

Sulfur dioxide (SO_2)—Is a colorless toxic gas with a stifling smell that is released during volcanic activity and produced in the burning of fossil fuels contaminated with sulfur compounds. It is one of the main atmospheric gaseous pollutants. Its reactivity with other substances in the atmosphere causes a wide variety of health and environmental negative effects, such as respiratory diseases, vision impairments, acid precipitations that damage buildings and plants, etc. Excessive exposure to SO_2 causes problems to eyes, lungs and throat [114,115].

Volatile organic compounds (VOCs)—Are a wide group constituted by carbon-based organic compounds (among them halogenated compounds, aldehydes, alcohols, ketones, aromatic compounds, and others), that easy evaporate in ambient condition [116]. VOCs are one of the major contributors to air pollution and their emissions from outdoor and indoor sources are growing due to rapid industrialization and urbanization. High concentrations of VOCs can cause health disorders or serious disease as cancer [117]. VOCs are also present in small concentration in human breath and they could be used as natural biomarkers to medical diagnosis [116]. Some of main VOCs are described below:

Methane (CH_4)—Is odorless colorless tasteless, no toxic but flammable. It results from decomposition of some organic compounds in the lack of oxygen. It is extracted from underground deposits, where it is often combined with other hydrocarbons. Primarily, it is used as fuel in home activities and in automotive field. It is a greenhouse gas, whose most important emission sources are the decomposition of landfill waste, the extraction from fossil fuels, and the digestive process in animals (livestock). In breath analysis it is a biomarker associated with lactose intolerance [95,117].

Ethylene (C_2H_4)—Is a colorless gas with a slight sweetish smell and extremely flammable. It is used by chemical industry as raw material to produce other VOCs and various plastic materials (e.g., polyethylene). Furthermore, it is involved in the ripening process of climacteric fruits. Ethylene can be thought as a hormone that triggers the ripening process of fruits, and also as an indicator that fruit is ripening. Indeed, keeping suitable concentrations of ethylene during fruit storage it is possible to speed up or slow down ripening [4].

Isoprene (C_5H_8)—Is a colorless liquid and with a characteristic odor. In industry, it is used mainly to produce polymeric compounds. It is the major hydrocarbon found in human exhaled breath, ranging

from 12.71 to 227 ppb in healthy human subjects. Its level increases naturally in human subjects with age and during physical activity. A high concentration is also correlated with chronic kidney disease (CKD) and other pathological states (hemodialysis, general anesthesia, liver disease, and cancer) [118,119].

Benzene (C_6H_6) and *Toluene (C_7H_8)*—Are colorless, toxic and carcinogenic liquids, with characteristic odor, that are naturally present in petroleum products and are subsequently released in the atmosphere during the incomplete combustion in road traffic. They are used in chemical industry and as solvents for paints, gums, adhesives, etc. These gases are responsible for the ozone layer reduction, they produce photochemical smog and they cause uneasiness at low-level of exposure, unconsciousness, dizziness, and even death at high level of exposure [116,120].

Formaldehyde (CH_2O)—Is a colorless, corrosive, flammable toxic and carcinogenic gas. It is known as formalin in water solution. Formaldehyde is a powerful bactericide used to make disinfectants; it is used as a food preservative and in the industrial textile dyeing. However, it is mainly used in the production of polymers and other materials employed to build handwork, coatings and insulating foams that release over time molecules of formaldehyde in the environment. Formaldehyde is one of the most widespread indoor pollutants, with no effects on health up to 0.1 ppm; at higher concentrations it irritates mucous membranes and eyes, up to become potentially lethal. It is a potential breath marker for lung cancer [121].

Acetone (C_6H_3O)—Is a colorless flammable liquid, with an irritant characteristic odor. It is primarily used as a solvent, also at industrial level. It is a natural biomarker associated with some metabolic diseases, like the diabetes (few hundred of ppb in healthy people, more than 1 ppm in diabetic subjects) [83].

Ethanol (C_2H_5OH)—Colorless, alcoholic smell and taste, flammable, low toxicity liquid. Produced in nature by sugar fermentation, it is the most widespread alcohol, and the only one suitable for food use. It is used as alternative fuel, as disinfectant and as s solvent for resins and paints. Most swallowed ethanol is metabolized in the body, while a small amount is eliminated through the urine, the sweat and the breathed air. It represents a natural biomarker related to alcohol consumption [122,123].

Liquefied petroleum gas (LPG)—Is a fossil fuel composed by a mixture of hydrocarbon gases, broadly employed in domestic environment and industry, to generate electricity, power heating systems, or cooking. It is also used as vehicular combustible. It is a highly flammable gas and dangerous because a leakage could result in ignition and explosion [124,125].

Sulfur hexafluoride (SF_6)—Is a colorless, odorless, transparent and not flammable gas. It is not considered as toxic gas and it is used in industry as electrical insulator because of its capability of extinguishing electrical arcs in high tension [126]. However, it is one of the six gases responsible of greenhouse effects covered by the Kyoto Protocol. SF_6 easily hydrolyses into fluorinated compounds in water that are extremely toxic and corrosive.

Chlorine (Cl_2)—In gaseous state has a strong odor and it is extremely toxic. It is largely used in the chemical and pharmaceutical industries, water treatments, in domestic cleaning products and also as chemical warfare agent. Threshold secure limit is about 30 ppb, 50 ppm can damage the respiratory system and levels of 1000 ppm can cause death [127,128].

Radon (Rn)—Is colorless, odorless and radioactive gas with a half-life of about 3.8 days. It derives from the decay of radium and uranium and it is naturally emitted from soil and rocks and transported through water, or environmental carrier gases. It represents half of the radiation exposure to human being and a long-term contact could induce lung cancer [129–131].

6. Conclusions

Flexible electronics, nanomaterials and polymers are the basis of the future generation of sensors. Indeed, with the advent of flexible electronics, sensors have become low-cost, thin, with large sensing area, lightweight, wearable, flexible and transparent, and therefore the number of new produced devices have multiplied as well as their applications in many aspects of our daily life. The sensor

demand, related to the IoT world, has stimulated the development of new sensor solutions as well as the mass production. In the coming years sensors will spread throughout the IoT world to monitor parameters related to human healthcare, to the environment, to machine operation, to food quality, to security, etc., and essential to have "smart things".

Printing is the most used technique to produce flexible electronics and flexible sensors due to its great number of advantages, such as mass production, low costs and the opportunity to implement different functional materials in to the ink. Among the printing techniques, inkjet printing is the most used, while to realize mass production the new R2R approach is preferred and is rapidly growing. The integration of different fabrication techniques in a single production line comprising the control electronics, data processing and transmission will enable low-cost applications in the emerging scenarios. R2R ideally enables this integration, however additional efforts should be profuse to successfully achieve the target.

In this review, the study of the current state of research and development of the printed chemiresistive gas sensors has confirmed the global trend regarding sensors and flexible sensors. Among the flexible substrates, polymer bases (PET, PI, etc.) are the most common, although there are some papers about gas sensors printed on paper or textiles. The choice of the substrate material is one of the main steps to fabricate a flexible sensor, because it has to be compatible with the device operational conditions and it affects directly the sensing performance. As for the rigid substrates, the functional materials range from metals, metals oxides, carbon nanotubes, graphene, graphene oxide, and conductive polymers. They are usually mixed to obtain better sensibility, selectivity, and reduced response and recovery times. A key factor to guarantee the durability and stability of the device is the coupling of the chemically selective layer to the physical part of the sensor, especially in developing flexible substrates-based gas sensors. A literature survey on the target gases related to the gas sensor applications has shown a great number of analytes correlated with many application fields. To date, printed flexible chemiresistive gas sensors covered only a few (H_2, H_2O, H_2S, NH_3, NO_2, CH_2O, C_2H_3OH, C_6H_3O) of the many target gases reported above. Besides the improvement of sensitivity, selectivity, response and recovery times, the development of new printed flexible sensors to monitor further gases down to low concentrations is the future perspective. The first use of chemiresistive gas sensors was the detection of explosive gases. Today, besides its application in environmental monitoring and in the industrial area, the major attention is paid to the control of human analytes, in order to prevent medical diseases and ensure safe, security and wellbeing.

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