Doctoral Dissertation
Doctoral Program in Electrical, Electronics and Communications Engineering
(34th Cycle)

# Electronic devices for room-temperature gas sensing applications

Lorenzo Vigna

## Abstract

Nowadays, climate change went from being a fringe issue to a global priority because its effects are less and less gradual, rushing headlong towards a suddenly point of no return. In particular, a key role is played by air pollution, which is sadly the leading cause of environmentally related severe health effects linked to cardiovascular and respiratory diseases. Every year the number of deaths by risks factors due to air pollution is over 8 million. To improve health status and life conditions of human beings, the first step is to improve enforcement of environmental regulations and ultimately achieving the zero-pollution ambition promoted by the EU. For tackling this issue, environmental monitoring is a topic of striking importance. Unfortunately, available analytical techniques employed in this field are often bulky, expensive, time-consuming and require expert technicians. Luckily, we are into the "Sensor century" and our daily life can significantly be changed by the development of high-efficiency electronic devices that can easily detect small traces of Volatile Organic Compounds (VOCs) and the other pollutants. Thanks to the miniaturized dimension and online measurements, they can be exploited as nodes to be employed in smart wireless sensor networks for the capillary monitoring of the territory.

Within this framework, the objective of the PhD dissertation is to illustrate the results of materials development and integration, characterizations, and device nanofabrication for gas sensing applications at room temperature. Chapter 1 and Chapter 2 introduce a brief overview on the state of the art of several existing gas sensors, defining the fundamental sensing parameters. Among all of them, chemiresistive gas sensors have been attracting growing interest. Indeed, chemiresistors are driven by the principle that upon exposure to the vapor to detect on the sensing material's surface, they are able to convert a physical phenomenon into a measurable signal, which is seen as a variation in the output electrical resistance. These devices are engineered to mimic and substitute human olfaction. Subsequently, three main material classes have been investigated: loaded conductive polymers (LPs), conjugated intrinsically conductive polymers (ICPs) and inorganic layered double hydroxides (LDHs). For each family, an in-depth analysis has been presented, followed by the selection of a representative sensing material, which led to the proper experimental investigations (Chapter 3). As a first step, a custom-built sensing setup able to generate and deliver selected concentrations of solvent vapors to the devices, housed in a detection chamber, has been completely engineered from scratch and validated. It has been necessary to be able to conduct real-time characterizations and acquire the sensing responses. Furthermore, the standard protocols applied to the sensing analysis are explicated (Chapter 4).

The first case study (Chapter 5) focuses on a new, flexible polymeric chemiresistor fabricated by UV-curing a photo-crosslinkable diacrylate resin (PEGDA) containing a dispersion of multi-walled carbon nanotubes (MWCNTs) as conductive filler. The one-step process enables to create an interpenetrated network from a liquid formulation. The best photo-curing conditions have been found in the presence of 0.3 wt% MWCNTs and 3 wt% of radical photoinitiator. The cross-linked self-standing film exhibits a percolative threshold conductivity, which explains the main transduction mechanism through the swelling of the matrix. The sensing response towards acetone is the smallest, while EtOH, IPA and water vapor display a similar behavior due to the presence of polar groups. Nonetheless, the best performance has been measured towards toluene. Further improvements could be reached by a simple modification of the photocurable formulation, tailoring the chemistry of the mixture and therefore the affinity towards polar or non-polar solvents.

The second experimental contribution (Chapter 6) is an in-depth investigation on conjugated PEDOT:PSS, which has been exploited as liquid formulation for the fabrication of resistive gas sensors by means of an ink-jet printer. Enhanced electrical conductivity and improved sensing performances have been obtained by submerging thin films in $H_2SO_4$ with different concentrations and pure MeOH. The post-treatments work as a simple, yet robust method for the irreversible secondary doping of PEDOT. In both cases, the conductivity has been enhanced due to the combination of different effects, namely the chain linearization from a random coil structure, the increased doping level by means of further oxidation and the removal of insulating PSS chains, which causes a better connection of the PEDOT domains. Real-time measurements have been carried out by exposing the devices to VOCs vapors in a low concentration up to 5% of the saturated vapor pressure, 10 ppm of $NO_2$ and up to 10% of relative humidity (RH) at room temperature. An unexpected behavior of PEDOT:PSS post-treated with concentrated $H_2SO_4$ has been observed, but the secondary doping appears to be detrimental concerning the sensitivity. MeOH and diluted $H_2SO_4$ post-treated chemiresistors, on the other hand, have exhibited good response towards all investigated analytes. In addition, long-term stability and the influence of temperature have been evaluated on the fabricated devices. Altogether, these encouraging results allow a better understanding of the secondary doping effects on the electrical and sensing properties.

In the third case study (Chapter 7), LDHs have been successfully synthesized through a coprecipitation method. For the first time, [Zn-Al−Cl], [Zn-Fe−Cl], [Zn-Al− $NO_3$] and [Mg-Al−$NO_3$] have been compared to investigate the sensing performances. The gas measurements outline that all of the LDH-based devices can reversibly detect acetone, EtOH, $NH_3$, and Cl vapors, reaching significant sensing response values up to 6%. Furthermore, the good gas sensing performance at room temperature can be associated to the peculiar morphology of the lamellar material, characterized by a 3D hierarchical flower-like structure. The high porosity and large surface area of this architecture enables several diffusion channels, responsible for a fast diffusion of the target molecules, and it improves the number of active sites available for the absorption both on the inner and outer surface of the nanomaterial. The results demonstrate that by changing the LDHs' composition, it is possible to modulate the sensitivity and selectivity of the sensor, helping the discrimination of different analytes.

In addition, under the common leitmotiv of air quality monitoring and the detection of specific pollutants such as particulate matter (PM), a special focus has been dedicated to present the European project AEROMET II, regarding the development and fabrication of reference materials for cascade impactors coupled with mobile total reflection X-ray fluorescence (TXRF) spectrometers (Chapter 8). With this intent, a simple parylene C microstencil technology has been developed, allowing a flexible direct patterning of acrylic discs otherwise impossible with conventional photolithography procedures.

Scientific improvements have been achieved concerning both the solid understanding of the sensing mechanisms that affect different chemiresistors and relationships amid chemical and physical properties related to the sensing response and performances. The investigated chemiresistors have exhibited an excellent palette of sensing performances. For the above-mentioned reasons, they can be suitable for the implementation of portable gas sensor arrays thanks to their small size, low power consumption and low operating temperature. By carefully embedding many single units characterized by different LDHs compositions and exploiting the secondary doping to have a dual nature of PEDOT sensors, it is possible to tune the response and implement a selective and reliable electronic nose prototype, able to detect the fingerprint of a broader number of specific vapors at very low concentrations at room temperature.

In conclusion, the whole PhD thesis has been thought as a small contribution to a bigger framework to take urgent action in order to combat climate change and its impacts, supporting the Sustainable Developing Goal 13 to fulfill the targets on the agenda, which are to be achieved by 2030.