Gas Sensing with Two-Dimensional Materials Beyond Graphene

L. Filipovic and S. Selberherr

Abstract—The semiconductor industry is intensely working towards the functional integration of devices beyond digital logic, such as sensors and RF circuits, on the same chip. For gas sensors, this requires that future devices can be fabricated with the same technologies as future digital logic transistors, likely using mature complementary metal oxide semiconductor (CMOS) fabrication techniques, due to the inherent low costs and scalability they offer. While chemoresistive semiconductor metal oxide (SMO) sensors have garnered significant attention in the last decades, resulting in their commercialization, they require high temperatures to initiate the surface chemical reactions for sensing, meaning that a complex integration of a microheater on a MEMS structure is required. This is not ideal and room temperature solutions are readily sought after. Two-dimensional (2D) materials appear to offer precisely that: Potential for integration with CMOS technology, while also being highly sensitive to many relevant gases at room temperature. This manuscript explores several types of 2D materials which have the potential to be used as channel materials in digital logic transistors and sensing films, due to the presence of a relatively wide band gap. Therefore, this excludes graphene from our discussion and we look into recent gas sensing trends with reduced graphene oxide, transition metal dichalcogenides (TMDs), and phosphorene and arsenene.

I. INTRODUCTION

The way in which we perceive the environment around us is heavily influenced by the molecular makeup of the air we breathe, or the presence of various gas molecules in our vicinity. Our noses are quite efficient in the detection of many different smells resulting from the presence of certain gases, but they fail entirely in sensing the precise gas concentration and in the detection of poisonous gases which do not give off a specific odor, such as carbon monoxide (CO). The Environmental Protection Agency (EPA) classifies six pollutants as the main sources of air pollution, mainly ground-level ozone (O₃), particulate matter (PM₂.₅ and PM₁₀), carbon monoxide (CO), lead (Pb), sulfur dioxide (SO₂), and nitrogen dioxide (NO₂) [1]. Most hazardous gases are only harmful above a certain concentration, which is why many governments and organizations place regulations and limits on the amount of these pollutants with the aim of reducing the inherent risks to humans and the environment [2].

Having the ability to detect these and other harmful and toxic gases in the atmosphere is of extreme importance for a diverse range of applications and industries. Among them, the most important are environmental monitoring [3], [4], [5], health and safety [6], automotive and transport [7], chemical warfare detection [8], and many more [9]. The European gas sensor market share by end-use is shown in Fig. 1, where we note that the applications are quite evenly spread across several industries and no single application is fully driving the development [10]. It is evident that industry requires sensors to detect a broad range of pollutants at varying concentrations. Gas detection has been a topic of interest for many decades and, prior to the application of gas sensors, animals were used for sensing of certain gases: A common example is the use of a canary for gas detection in mines, as it stops singing once exposed to methane, carbon monoxide, or carbon dioxide. The current gas sensor market is estimated to be worth between one and two billion Euro with an annual growth rate of about 5%-10% in the next decade [10], [11].

![Fig. 1. Europe gas sensor market share by end-use in 2020 (source: https://www.grandviewresearch.com).](https://www.grandviewresearch.com)

The predicted gas sensor market expansion comes from the increased need for gas sensor integration with vital communication technologies to enable the aggressive advancement of Internet of Things (IoT), Internet of Everything (IoE), cloud computing, etc. IoT is a multi-layer technology which connects diverse hardware – smart appliances, smart gadgets, wearables, and mobile consumer devices, all of which are equipped with sensors – together with the Cloud of Things (CoT) [12]. The most significant hurdle to a widespread integration of gas sensors is their price, so the increased application of these devices will only be enabled by unit cost reduction which is achievable through sensor miniaturization and integration with signal drive and process-
ing circuitry [13]. This most often means the use of solid state and semiconductor-based gas sensors with integration with a low-cost and mature manufacturing technology, such as complementary metal oxide semiconductor (CMOS) fabrication [9], [14].

In this manuscript, we summarize some key features of available gas sensor technologies, while concentrating on semiconductor-based sensors with the highest potential for miniaturization and CMOS integration. This ultimately leads towards the conclusion of the highly-likely introduction of two-dimensional (2D) materials in sensing devices in the near future.

II. GAS SENSOR TECHNOLOGIES

The requirements for today’s sensors for IoT are quite ambitious and must exhibit several excellent features and properties, such as [13]:

1. Low cost of fabrication and operation
2. Low power consumption
3. High reliability and repeatability
4. Real-time communication capability
5. High data security

A broad selection of different types of gas sensors are currently being investigated at different levels of research and development. Some mature gas sensing technologies, already implemented in industry, includes semiconductor-based, catalytic pellistors (CP), piezoelectric (PE), electrochemical (EC), thermal pellistor (TP), photo-ionization (PI), and infrared (IR) adsorption [9], [15], [16], [17]. These sensors are commonly more broadly classified into two groups, those whose transduction is based on a change in a film's electrical properties (e.g., conductivity) and those whose sensing is based on changes in other properties (e.g., optical, thermal) [18].

From these options, the semiconductor-based semiconductor metal oxide (SMO) sensor presents a solution with the lowest power, cost, and footprint, by virtue of its integration with CMOS fabrication technology. These properties are essential in order to provide a sensing solution for portable application and IoT integration, while CMOS integration also provides a means for excellent reproducibility [19]. For mass production of commercial devices, it is critically important that the variations in the structure are minimal and that there is a high confidence that predictable device properties will be fabricated, with well controlled tolerances. We note that the catalytic pellistor also operates with a low power consumption and can be fabricated at low cost with a relatively small footprint. However, the selectivity of this device is very poor, its sensitivity is weaker, and the response time is longer than that of an SMO sensor. A high sensitivity is provided by the piezoelectric, photo-ionization, and infrared sensors, but they all have some concerns, when it comes to their power consumption as a limitation to portability.

As alluded to earlier, in order to provide enough energy and to enable the oxidation-reduction reactions on the SMO surface, the SMO sensor needs to operate at elevated temperatures, in the range between 200°C and 550°C [9]. This elevated temperature means that the sensor must be integrated with a microelectromechanical systems (MEMS) microheater element, which should also be thermally isolated from digital, analog, and radio-frequency (RF) components [25], [26]. The increased complexity in the sensor’s geometry is another potential concern with the long-term thermomechanical stability of the device, as it relies on a suspended membrane which hosts the microheater and the...
sensing film [27]. The constant heating and cooling of the device can lead to a build-up of thermally induced mechanical strain, ultimately resulting in cracking, delamination, and the complete mechanical failure of the sensor. Therefore, researchers are actively investigating the potential of providing a semiconductor-based CMOS-integrated conductometric gas sensor solution which can operate at room temperature and improve the selectivity and specificity towards gases of interest [22], [28], [29], [30]. Two-dimensional (2D) materials, such as graphene and TMDs have shown some promise for room temperature gas sensing, primarily due to their inherently high surface-to-volume ratios [6], which enables a very high surface exposure and thereby a high sensitivity and response to changing ambient conditions.

III. 2D SEMICONDUCTOR GAS SENSORS

Research into different semiconductor films for gas sensing applications has been very intense for several decades. While the initial interest arose from bulk SMO films, discussed in the previous section, more recently, due to their need for operation at elevated temperatures and poor selectivity, research has moved into SMO nanostructures [31], conducting polymers [32], carbon nanotubes [33], and most recently 2D materials [5], [34]. An overview of the different semiconductors films studied for applications in gas detection is presented in Fig. 3 [13]. Other than metal oxides (SMOs), the materials depicted are still in the research phase and no commercialization has, as of yet, taken place.

![Fig. 3. Semiconductor materials which have shown a propensity for application in gas sensing. (Source: Nikolić et al. [13])](image)

The application of conducting polymers in industry is hindered by the complex and time-consuming fabrication requirements [35], while, due to oxidation, the lifetime of gas sensors based on these films is significantly shorter than SMO-based sensors [13]. Carbon nanotubes (CNTs) are cylinders which are formed by wrapping graphene sheets along the axial direction [36]. These films have a good chemical and mechanical stability, suitable electronic properties, and a high surface to volume ratio [37]. However, their future applicability may be hindered by a costly synthesis, as it is very difficult to grow continuous defect-free nanotubes, and their fabrication is not compatible with CMOS technology [38], [39]. Another concern is a lack of selectivity and specificity, since the CNTs readily interact with oxygen and water molecules, which influences the sensor response. The ideal gas sensing solution of the future should be compatible with future CMOS transistor technologies. This would allow for easy integration of the sensing element with digital and analog electronics, while also making the fabrication of the sensing devices compatible to mass-fabricated low-cost digital transistors which drive the microelectronic industry. With this in mind, 2D materials appear to have the most optimistic outlook for application in real devices and commercialization in the near future.

In this manuscript, we also exclude graphene from our discussion. Studies which demonstrate the potential of graphene and other 2D films to be used as gas sensors by showing a change in the resistance of the film under exposure to one or several gases are plentiful. The Nobel laureates for fabrication and characterization of graphene (Geim and Novoselov [40]) reported on graphene’s high sensitivity to the presence of NO2 and NH3 [41]. However, research into graphene has struggled to provide a working field effect transistor (FET) due to its lack of a band gap, so other potential 2D materials have risen in prominence, which display a band gap and have significant potential for simultaneous FET and sensor applications. In this section we examine these materials, including graphene oxide, TMDs such as MoS2 and WS2, phosphorene, and arsenene for gas sensing applications.

A. Graphene Oxide and Reduced Graphene Oxide

As previously mentioned, graphene has attracted considerable attention for applications in sensing and FETs, likely due to being the first fabricated and investigated monolayer film. However, its quasi-zero band gap presents a hurdle in its broad applicability in transistors and sensing devices. Therefore, many researchers started to investigate functionalized or decorated graphene using graphene oxide (GO) [42]. GO can be fabricated by treating graphite with strong oxidizers which causes the separation of graphite from GO flakes. By exfoliating the graphite, single layer GO flakes remain [43]. Hummers’ method has been extensively used to obtain less defective and wider GO flakes in order to increase the yield of production [44].

Graphene oxide (GO) flakes have been readily applied in the detection of relative humidity (RH) with an impedance sensor [45]. In these studies the real
and imaginary parts of the dielectric constant of the GO flakes serve as the sensing signal [46]. As the dielectric constant changes due to adsorption, the frequency response is varied and a shift in the resonant frequency can be observed. This was recently applied in a piezoelectric micromachined ultrasonic transducer with a GO sensing layer for fast and precise RH detection, shown in Fig. 4 from [47].

Conductometric gas sensing devices using GO flakes as a transducer show very little change with increasing humidity [43], [48]. This is a very positive development in terms of the application of gas sensors for disease detection. The dependence of humidity on the sensitivity is the biggest challenge for sensor integration into real-world medical diagnostics, especially for breath analysis, which contains at least 80% humidity [49]. For example, conductometric GO sensors have shown a selective detection towards NO\textsubscript{2} in a humid ambient [50], giving hope for the application of these devices in future medical applications. The relative response was shown to not vary at all when increasing the RH from 50% to 75%, values, highly relevant for breath detection. The ability of GO to detect NO\textsubscript{2} is primarily related to the oxygen functional groups on the GO surface, as it was shown that graphene and reduced graphene oxide (rGO) do not show high responses to NO\textsubscript{2} [51].

To increase the sensing performance and selectivity/specificty towards a particular gas, researchers have studied modifying the GO surfaces by functionalizing or micromachining [43]. Surface functionalization has already been applied to SMO sensors and is a common means to slightly vary the chemiresistive gas sensing performance of semiconductor films. For example, tailored GO flakes have been fabricated for increased detection of SO\textsubscript{2} [52] and NH\textsubscript{3} [53] at room temperature.

The resistivity of GO films is quite high, so to partially restore some of the high conductivity of graphene, the GO films are commonly reduced, obtaining rGO flakes [42]. These flakes have been heavily investigated for application in gas sensing due to their high conductivity and the presence of residual hydroxyl groups on their surface, which promote adsorption [43]. The degree of reduction can also be controlled and tuned in order to tailor the film towards a particular application. These films have been shown to detect many relevant gases and chemicals at room temperature. Some examples include the detection of chemical warfare agents at the ppb level [54], NH\textsubscript{3} at concentrations from 5 ppb to 100 ppm [55], NO\textsubscript{2} at ppb levels [56], [57], or hydrogen at ppm levels [58], [59]. Recently, Wang et al. [60] have studied a hybrid rGO-graphene sensor for highly-selective ammonia detection, with results shown in Fig. 5. The four sensors studied are based on rGO and graphene hybrids, where the reduction times of the rGO layer are 0, 10, 20, and 40 minutes for sensors 3-1, 3-2, 3-3, and 3-4, respectively [60]. The results show a strong selectivity towards NH\textsubscript{3} for all reduction times, while the highest sensitivity is shown for the case with the smallest non-zero exposure time of 10 minutes. Coupling the sensing performance of rGO films together with SMO nanostructures has also shown promise in the synthesis of highly sensitive and specific gas sensors, albeit with a significant increase in the fabrication complexity [61], [62].

B. Transition metal dichalcogenides

Interest in 2D TMDs has increased dramatically in recent years and several academic groups have successfully fabricated transistors using these thin layers [63], [64]. Among TMDs, molybdenum disulfide (MoS\textsubscript{2}) [64] and tungsten sulfide (WS\textsubscript{2}) [65] are of particular interest for devices, because they are naturally occurring layered crystals with a wide band gap, are robust, and relatively abundant. While research is ongoing to find the most appropriate insulator for top-gated and back-gated 2D FETs in order to minimize interface defects [66], the back-gated design is desired for sensing applications, as it allows to control the electrostatics in the conductive TMD channel, while its surface is fully exposed to the ambient, depicted in Fig. 6 [67].

MoS\textsubscript{2} and WS\textsubscript{2}, in their bulk forms, are constituted of...
several S-Mo-S or S-W-S planes, respectively, bounded to each other by weak van der Waals forces. These films can be exfoliated down to a monolayer or they can be synthesized by chemical vapor deposition (CVD) [68]. The bulk MoS2 and WS2 films are indirect semiconductors with band gaps of 1.2eV and 1eV, respectively. The monolayer versions of these films are direct semiconductors with band gaps of 1.8eV and 2eV, respectively [69].

MoS2 transistors have shown to respond to a broad range of gases at room temperature such as, H2 [70], O2 [71], NO [72], NO2 [73], NH3 [74], and many more. Humidity and oxygen are specifically very prone to reactions with MoS2 and can be hindrances to the broad applicability of MoS2 in future electronic devices due to their high concentrations in air and in exhaled breath [49]. Furthermore, polycrystalline MoS2 films are especially burdened by high defect concentrations on edges and grain boundaries, where gas molecules can frequently adsorb [75], [76].

Many recent studies have confirmed the potential for room temperature chemical sensing using TMDs, especially MoS2 and WS2 [77]. Monolayer MoS2 on a SiO2/Si substrate has been used to sense triethylamine (TEA) down to few ppb selectively against many other analytes [78], c.f. Fig. 7. Further research has shown an excellent response for the monolayer MoS2 detection of NO2 selectively in an ambient which includes H2, H2S, and NH3 [79] or C2H5OH [80]. Several studies also confirm the ability of many TMDs to detect relevant gases, including humidity, NO, NO2, NH3, H2, CO, and many more [43], [77]. It is important to note that for non-polar gas molecules (e.g., CO2 and CH4) the pristine MoS2 surface does not offer strong adsorption and thus does not support gas sensor applications. However, in the presence of defects, and most commonly the sulfur vacancy, the interaction between the gas molecules and vacancy sites promotes the adsorption and induces a resistive change in the film [81].

C. Phosphorene and Arsenene

Phosphorene is the monolayer of black phosphorus, which has a honeycomb structure, a high carrier mobility and a band gap which ranges between 0.3eV and 1.9eV with a p-type conductivity [82], [83]. Similar to TMDs, black phosphorene has already been used to fabricate and test FETs [84] and it has been applied towards gas sensing applications [85]. Using ab-initio density functional theory (DFT) calculations, it has been shown that, when adsorbed on the phosphorene surface, CO, H2, H2O, and NH3 molecules act as electron donors, while NO, NO2, and O2 act as electron acceptors [86]. NO2 has the strongest interaction with the phosphorene surface, suggesting its potential in future gas sensing devices [43]. Experimental observations in [85] indicate that a black phosphorus based FET is able to detect down to 5 ppm NO2 in an argon atmosphere, while the response time of the device was very slow, on the order of a few minutes. The recovery time was even longer, about 30 minutes.

Cho et al. in [87] recently reported on the difference in response to NO2 for various 2D films, including MoS2, rGO, and phosphorene at room temperature. They found that the phosphorene sensor had a significantly higher sensitivity response, when compared to rGO, and a slightly higher response than that of the MoS2 film. What made the phosphorene stand out, when compared to MoS2, was that its selectivity towards NO2 surpassed that of the MoS2 film, depicted in Fig. 8. More recently, there has been an interest in
blue phosphorene, a new allotrope of black phosphorus, formed by a single layer of more flatly arranged phosphorus atoms [88]. Blue phosphorene has a carrier mobility of over 1000 cm$^2$V$^{-1}$s$^{-1}$ [89] (in comparison, the mobility of MoS$_2$ is about 200 cm$^2$V$^{-1}$s$^{-1}$). Blue phosphorene also has a fundamental wide band gap of about 2 eV, which can be modified to a direct band gap by doping [90].

![Fig. 8. The maximum resistance change in different 2D films, when exposed to various analytes, showing a selectivity towards NO$_2$. (Source: Cho et al. [87])](image)

Another 2D material of interest to sensing is arsenene which is a honeycomb monolayer of arsenic [91]. The monolayer of arsenene has an indirect wide band gap of about 1.62 eV [92], which can be transformed to a direct band gap by applying biaxial strain [93]. Research on this material is still in its infancy and little to no experimental observations are available, but theoretical results using ab-initio DFT suggest that this material has a promising application in NO sensing due to its strong sensitivity and selective response to the presence of NO molecules [94]. Arsenene was also shown to be highly sensitive to the presence of nitrogen-containing gas molecules such as NO and NO$_2$ using theoretical first-principles studies [95].

**IV. CONCLUSION**

In this manuscript, we look at the progress and current state of research into semiconductor-based gas sensors, specifically concentrating on technologies which have a high potential for CMOS integration such as those based on 2D materials. The current semiconductor gas sensor workhorse is the SMO film, but it requires high temperatures to initiate the sensing mechanism, meaning it suffers from complex fabrication and is prone to high mechanical instability. Room temperature alternatives are sought after, where 2D films appear to be most promising. Their extremely high surface-to-volume ratio ensures that their sensitivity is very high even at room temperature. Nevertheless, some persisting problems still must be addressed prior to their broad application and commercialization.

The lack of band gap in graphene has resulted in research being shifted towards other 2D films which include graphene-based films such as GO and rGO, TMDs, and other materials such as phosphorene and arsenene. GO and rGO appear to be the closest to production, but some effort is still required before devices based on these films can be efficiently mass produced with a predictable device behavior. Reduced graphene oxide especially requires the oxidation of graphene followed by the removal of some oxygen atoms, which can be very imprecise. TMDs are currently thought to be the future of digital transistors and sensing and significant progress has been made in recent years towards the predictable and repeatable synthesis of these materials using CVD. A major problem with these films is that pristine films have a relatively low carrier mobility which is increased by introducing defects. However, the introduction of defects comes with a host of other problems, such as modifications of the film’s behavior due to undesired interactions with the ambient. It is also still not fully clear, how defects affect the conductivity, so further studies are still needed. Research studies into phosphorene and arsenene are still in their infancy and are mostly based on first principles calculations. Nevertheless, these films are promising for the selective sensing of nitrogen-containing gas molecules. There are ample benefits of 2D films over bulk materials for gas sensing and more research and collaboration between experimental and theoretical groups are needed to truly tap their full potential.

**REFERENCES**


Fig. 8. The maximum resistance change in different 2D films, mobility of over 1000 cm$^{-1}$ and phosphorus atoms [88]. Blue phosphorene has a carrier concentration of blue phosphorene, a new allotrope of black phosphorus, with a fundamental wide band gap of about 1.5 eV, making it a promising candidate for gas sensing and other applications.

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What determines our choice?

Gas Sensors

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