Fire gas detection

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Abstract

Most but not all fires emit smoke aerosols at some point during the combustion process. Therefore most conventional fire detectors are based on the detection of smoke by light scattering. As every fire is emitting specific gases it is reasonable to upgrade photoelectric fire detectors or even replace them for specific environments with gas sensor based technologies. In this paper we present some gas detection technologies which have the potential to be able to amend or replace existing systems for use especially in residential fire detectors. But here some restrictions apply when using gas sensors. Among others these are low cost, low power and long term requirements. We identified advantages but also some challenges of gas detection technologies by testing colorimetric gas sensors, gas sensitive field effect transistors and metal oxide sensors. As most technologies are not completely selective to the target gas and as there is not “the” fire with one specific mixture of combustion gases it is helpful to combine different sensing elements in sensor arrays where algorithms using pattern recognition methods like PLSDA, PCA etc. can be used to increase the prediction reliability and the false alarm robustness. Here we focused on typical combustion gases like CO, CO2, NO, NO2, NH3 and H2.

Keywords: Metal oxide, SnO2, GasFET, fire detection, PLS, pattern recognition, combustion.

1. Introduction

The first automatic smoke detector invented in 1940 was based on the measurement of the ionization current using americium-241 as a radioactive source [1]. The alpha radiation emitted ionizes oxygen and nitrogen in the air in the sensing chamber leading to a measurable ionization current which decreases when smoke particles are present. Although these materials are relatively safe in use the acceptance at

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least in Europe decreased in the past. Environmental and health issues occurred and using radioactive sources in fire detectors became undesirable. Although ionization detectors are still more sensitive as conventional photoelectric detectors (“point detectors”) nowadays most residential fire detectors are based on smoke detection by light scattering using forward scattering and/or backward scattering combined with the detection of heat. Some use multiple wavelengths (IR and blue) to decrease the detection limit and to suppress false alarms which in most cases are due to dust or water vapor. For specific environments there are also alternative techniques in use like flame detectors, linear optical detectors, aspirating smoke detectors and linear heat detectors (using raman scattering in optical fibers) – to name just a few.

Not all fires are emitting smoke (pure ethanol fires for example do not) and especially some hot open fires do not emit bigger quantities of smoke. But combustion gases are emitted from every fire and their detection can be helpful for an early fire detection. There are numerous different gaseous compounds which are emitted during a “normal” fire in buildings. Depending on the type of fire and the different materials which are used in furniture, toys and the building construction, gases like CO, H₂, NO₂ and CO₂ but also HCl, HBr, HCN, Ammonia, Acrolein, SO₂ and many others may occur. Surprisingly during a fire most people do not die from heat or flames but from poisonous gases [2]. For residential fire detection some requirements apply restricting the choice of sensor technologies. Among others there are:

- Low cost requirements (below 5 Euro), mass production
- Self control ability
- Power consumption 1 mW or less (a whole fire detection panel including detectors has to have a battery back up for at least 72 hours). Modern stand alone battery operated point detectors run for up to 10 years with one battery!
- Small dimensions (to be included in existing detector housings and sockets)
- Sensitive to target gases like CO, CO₂, NO₂…
- Low cross sensitivity to interfering gases (humidity, alcohol, detergents, cooking fumes…)
- Low drift
- Fully reversible (standardization and test procedures)
- Lifetime > 10 years, long term stability of sensors.

Therefore the number of different gas sensing technologies is very limited and several attempts have been made in the past to develop and include gas sensors in fire detectors. For example in the past electrochemical CO-cells have become small, cheap and robust enough and several products were launched on the market. But not only technical reasons hindered the implementation of gas sensors. Due to regulations and standards today according fire detectors are not allowed to work on gas sensors alone (EN54 standard). In order to be robust against nuisance, gas-only based fire detectors should detect at least two typical combustion gases simultaneously and there are several arguments to go for an according development. With respect to photoelectric detectors most false alarms are due to dust and water vapor and it can be expected that fire detectors using several gas sensors as basis for pattern recognition algorithms will help to improve the overall detector performance like:

- Earlier alarm, less false alarms (dust, water vapor)
- Investigation of fire history (arson, information for insurances)
- Access to additional information. Detection of fire accelerators and combustible gases (natural gas, solvent vapors, gasoline…) – prior to fire events
- Distinguishing between different fire types (open- and smoldering fires, specific chemicals, information to fire brigades)
- Providing additional information like air quality (humidity, carbon dioxide, volatile organic compounds).
- Serving additional life-safety applications (i.e. CO-detection)

One additional advantage of using gas sensors might be the comparably fast diffusion of gases through heat layers when compared to smoke aerosols. In this paper we focus on the investigation of three different gas sensor technologies which meet at least some of the above requirements. As an example, temperature cycled metal oxide sensors (SnO$_2$-hotplate), gas sensitive field effect transistors (GasFETs), colorimetric gas sensors (optodes) will be presented. The technologies are intended to work also as a fire detection system on its own – without the support of photoelectric systems.

2. Metal oxide sensors

Metal oxide sensors are well known since several decades and still are basis for comprehensive research activities. Among their advantages are their strong sensitivity to all type of gaseous compounds and their overall stability. Generally their limited selectivity can be a critical point for some applications. Since they have to be heated up to temperatures between 150°C and 350°C the power consumption was rather high. With the development of membrane setups (hotplate) and a resulting very low thermal mass it is now possible to operate them with a comparably low power consumption – even continuously. Changing the operation temperature leads to changing adsorption characteristics with respect to different gases. By applying short heat pulses the power consumption can be drastically decreased and additional information can be derived out of the signals. Gases can be identified even in the presence of others also reacting with the sensor surface [3], [4], [5].

Table 1: EN54 test fires and according gaseous compounds. Main target gases are in bold.

| Test-fire | Combustion material                        | Combustion products (target gases are bold)                                      |
|-----------|--------------------------------------------|----------------------------------------------------------------------------------|
| TF1       | Open beech wood fire (ignited with ethanol) | CO$_2$, CO, H$_2$, H$_2$O, NO, NO$_2$, methane, acetylene, ethane, styrol, chlorobenzene, ethanol, … |
| TF2       | Smoldering beech wood fire                 | CO, H$_2$, H$_2$O, CO$_2$, NO, HCl, methane, ethane, aromatic hydrocarbons: (benzene, toluol, xylene, styrol, chlorobenzene), acrolein, formaldehyde, formic acid, acetic acid, … |
| TF3       | Glowing smoldering cotton                  | CO, H$_2$, NO, CO$_2$, H$_2$O, methane, acetylene, ethane, benzene, acetaldehyde, formaldehyde, ethanol, … |
| TF4       | Open polyurethane foam fire               | CO$_2$, CO, H$_2$O, NO, NO$_2$, N$_2$O, HCN, NH$_3$, amines, ethane, styrol, acetone, … |
| TF5       | Open n-heptane fire (3%Toluol)            | CO$_2$, CO, H$_2$, H$_2$O, NO, NO$_2$, ethane, styrol, chlorobenzene, ethanol, octane-n-hexane, … |
| TF6       | Open ethanol/alcohol fire (liquid)         | CO$_2$, CO, H$_2$, H$_2$O, NO, NO$_2$, ethane, styrol, ethanol, … |

Table 1 lists standardized test fires (EN-54) and their main gaseous compounds. Gases like CO$_2$, CO, H$_2$, H$_2$O, NO and NO$_2$ can be found in any fire. Main compounds are CO and H$_2$ in smoldering fires whereas CO$_2$, and NO$_2$ are emitted in hot and complete combustion processes (open or flaming fires). Using appropriate sensors makes it possible to distinguish between those fire types. One apparent problem of metal oxides which often is stated is the different signal direction when exposed to reducing and oxidizing gases (CO and NO$_2$) because during fires both gases can be present and the signals could be
counterbalanced resulting in a zero signal. But by applying heat pulses to the sensor and using subsequent recognition algorithms – for example based on PLSDA (Partial Least Squares Discriminant Analysis) this problem can be solved. In this work we worked with SnO₂ hotplate metal oxide sensors (Applied Sensor, www.appliedsensor.com), applied heat pulses of 0.9s length and sampled 100 times per pulse.

Figure 1: Left: applied voltage, right: resistance (a.u.) during a fire event. 2.7V corresponds to 350°C. One cycle lasts 0.9s.

Figure 1 shows the applied heating voltage and the transient signal of the hotplate SnO₂-metal oxide sensor during a fire event as shown for example in Figure 2. After measuring a complete set of test fires we developed a suitable model for PLSDA by pre-extracting the most pronounced differences of signal shape. We were able to successfully test the model with respect to discrimination between open and smoldering fires. These signal evaluation algorithms need limited computation power in operation, so that it can be easily done by a low-power microcontroller (basically it is only one multiplication of a fixed matrix with an input vector containing measurement data). Figure 3 and Figure 4 show the according results. The strong sensor signal to solvent vapors (not shown here) which impose high requirements to the signal evaluation, however open up the possibility to the detection of accelerants giving the possibility to announce an according pre-alarm.
Figure 2: SnO$_2$-metal oxide sensor resistance at heatpoint 69 (refer to Figure 1) during different test fires (refer to Table 1) and nuisance events. Influence of ageing on sensor response.

Figure 3: Prediction of test data as “no fire” using a PLSDA-model. Very few of the fires get misinterpreted as no fire. Legend: red no fire – “no fire” before ignition and during weekend, green smoldering – TF2, blue smoldering – TF2 reduced intensity, light blue smoldering – TF3, grey smoldering – TF3 reduced intensity, red flaming – TF4, green flaming – TF4 reduced intensity.
Figure 4: Prediction of test data as “smoldering fire” using Model 1. The discrimination works well. Even the low-intensity fires are detected correctly. Legend: red no fire – “no fire” before ignition and during weekend, green smoldering – TF2, blue smoldering – TF2 reduced intensity, light blue smoldering – TF3, grey smoldering – TF3 reduced intensity, red flaming – TF4, green flaming – TF4 reduced intensity.

A background concentration of interfering gases and even the change of the environmental temperature changes the sensitivity to the target gases. As cross sensitivities to solvent vapors are pronounced a product development therefore needs a detailed investigation of interfering gases but also on drift, long term behavior of sensitivity and stability, humidity and temperature influence. The lack of discrimination power using just one sensor can be solved by using different sensing layers. Nevertheless power consumption has to be considered.
3. Colorimetric Sensors (Optodes)

Another approach to cost effective fire gas detection is given by materials which change their color during gas exposure. Compared to the well known materials which are used by the police to check alcohol content in breath the requirements in fire detection are different. Most of these applications use one-time disposable sensors whereas for fire detectors the change of color has to be fully reversible. For passing approval and certification procedures but also during regular tests of fire detectors in buildings a reversible reaction and stability for many years is indispensable. An according system needs a color changing chemical complex reversibly binding the target gas, a polymer matrix in which the complex is embedded and a substrate on which the color dye is deposited. The optical readout then can be done by using cost effective LED’s emitting in the appropriate wavelength (or nearby) and a photo detector. A wide range of different chemical complexes like azobenzenes, corrin, porphyrines, phtalocyanines, macrolides are described in literature for the detection of NH₃, CO₂, NOₓ, CO and other gases. Several investigations have been made and many patents were filed also for fire detection applications [6], [7], [8].

In this work we used a rhodium complex as the basic indicator substance for CO which is shown in Figure 5. Based on previous works [9] we exchanged the ligands with fluorathetic acid groups in order to make the complex less sensitive to humidity [10].

![Figure 5: rhodium complex which was used as CO indicator (left). Absorption in the UV-VIS range of the Rh-complex in solution without and with exposure to 100% CO (right).](image)

During exposure to CO there is an exchange of the axial ligands. Both fluorathetic acid groups can be replaced by one CO-molecule leading to a colour change. The most pronounced change of absorption was measured at 405nm and 562nm. The indicator substance then was embedded into a PVC matrix for stabilization and in order to be able to coat a glass substrate used as waveguide. The principal measurement setup and the measured change of absorption are shown in Figure 6. When embedded in the PVC-matrix the change of absorption at 405 nm nearly disappears. One half of a conventional glass substrate then was coated with the PVC-matrix stabilized complex where the second, non coated half was used as a reference channel. The layer thickness was between 50 nm and 300 nm. In order to be close to a
low cost future detector design we chose a conventional yellow LED (peak wavelength 590 nm) as emitter and a conventional photodiode (BPW 32) as detector (spectral range 350 to 1100nm). Figure 7 shows the results obtained using this measurement setup during different test fires in a 1m$^3$ test chamber.

Figure 6: principle measurement setup comprising a conventional yellow LED, a glass waveguide and two photodiodes (left). Change of absorption in the UV-VIS range of the Rh-complex in a PVC-based matrix during exposure to 100% CO (right).

Figure 7: measurement results of the detector setup shown in Figure 6 using the PVC matrix embedded Rh-complex during different test fires. The spike at 30 min is due to switching on the room light – after that the system was immediately covered by a protection.

The signals follow well the measured CO-concentration. The complex reacts reversibly, nevertheless a slight drift, which is possibly due to changes in ambient temperature influencing the electronics, can be observed. The sensitivity seems to be good enough for fire detection purposes. For a future product
development detailed investigations have to be performed especially on long term stability and the influence of humidity and temperature. It is known that such complexes suffer from bleaching effects which lead to premature ageing. One possibility to increase lifetime might be the use of very short light pulses for optical readout followed by longer inactive periods. As a reliable fire gas detection needs the ability of detecting additional gases like NO₂ the setup can be extended by using additional sensitive layers.

4. Gas Sensitive Field Effect Transistors

Another gas sensing technology for low power applications is the work function readout using field effect devices. Whereas first introduced with the hydrogen-sensitive field effect transistor with a heated Pd-gate by Lundström, recent developments focus on CMOS compatible suspended gate FETs (“GasFET”) [12], [13], [14]. The electrical potential that arises from gas adsorption at the sensitive material which is deposited on the gate is directly used to control the transistor characteristics. To allow gas access the gate is suspended by several μm from the isolating passivation layer to allow gas access. A schematic cross section is shown in Figure 8. Using appropriate sensing layers, these GasFETs work at room temperature and therefore have a low power consumption. In our case we used a floating gate device which recently has been industrialized by Micronas (www.micronas.com). As the FET is processed using standard CMOS manufacturing procedures all the needed readout electronic can be included on the same chip and even a microprocessor could be included in future.

Figure 8: Schematic cross section of a floating gate FET (FGFET) using a suspended gate. Gas molecules are able to enter the gap between sensitive layer and the passivation-layer above the floating gate electrode.

Several GasFETs channels can be operated in parallel and therefore different gases can be detected simultaneously which is the basis to implement pattern recognition algorithms. Materials which were tested here as sensitive layers were Pt, Ga₂O₃ (“GaOx”) copper phthalocyanine (CuPC), heteropolysiloxane (HPS) and TiN films, whereas also materials like BaTiO₃/CuO, SnO₂/Pd, polyvinylpyrrolidone (PVP), polyamide (PA) and others were reported [15]. We identified CO, H₂, NO₂ and NH₃ as a set of suitable fire gases to be tested. CO and H₂ are typical gases emitted during smoldering fires. They can be detected by Ga₂O₃- or Pt-films. NO₂ is mainly emitted from open fires and can be detected by the CuPC-films. NH₃ can be found in cigarette smoke as well as in acrylic wool combustion gases. CO₂ also is a typical combustion product but as it can be found also in human breath in higher concentrations we decided to not consider it for fire detection.
Figure 9: response of Pt-, Ga2O3- (GaOx), CuPC-, HPS- and TiN layers equipped GasFET’s to CO, NO2, H2, ethanol (EtOH) and CO2.

Figure 9 shows the response of 4 different GasFET’s to CO, NO2, H2, ethanol (EtOH) and CO2. None of the layers is responding to ethanol which is important for minimizing the false alarm rate. The CuPC-layer only shows response to NO2, whereas the TiN-layer is not responding to any of the measured gases but to NH3 (not shown here). The Pt-layer behaves similar to the GaOx-layer but with a higher overall response. Both are responding to CO, H2, NO2 but not to CO2 and ethanol. Beside the response of the HPS-layer to NO2 in opposite direction to Pt and GaOx, an interesting result is its response to CO2. During fire tests, concentrations of the gases of interest were recorded simultaneously using commercial gas analyzing systems. In addition, the optical absorbance (SICK) and an ionisation chamber (MIC, not shown here) were used as a reference. Figure 10 shows the signals of Pt-, GaOx-, CuPC- and TiN equipped GasFETs during a smoldering PVC-cable and an open (flaming) beech wood fire (TF1). The differences in signal strength and direction are due to the different gases which are emitted. It is likely that PVC emits HCl during combustion which causes a signal on the CuPC- and also on TiN-layer. The open beech wood fire mainly emits NO2. Figure 11 shows the response of the sensors to polyurethane fire (TF4) and to a smoldering fire (TF2). As during TF4 CO concentration is low (9 ppm after 90s) and that of NO2 (1 ppm after 90s) comparably high, the Pt and CuPC layers are reacting in the opposite direction compared to the smoldering fire (TF2) where the CO concentration is comparably high and that of NO2 low. By interpreting the different signals it becomes possible to identify different fire events. As elementary signal evaluation algorithms only may take signal slope and direction into account, PLSDA-based algorithms might give a deeper understanding of the fire situation and/or atmospheric conditions.
Figure 10: response of 4 different GasFETs, to smoldering PVC-cable (left) and TF1 (right) open beech wood fire.

Figure 11: response of 3 GasFETs to TF2 (right) smoldering beech wood and TF4 (left) polyurethane fire. The actual NO$_2$- and CO concentration is shown below. The optical attenuation is recorded by a SICK reference measurement system.

For the model creation we took the information from 4 layers (refer to Figure 10) and performed first of all a smoothing of all signals (Savitzky-Golay with a window of 40s). Afterwards the 1$^{st}$ derivative was taken to become independent of sensor baseline. Finally smoothing of the resulting data was performed with a window of 20s. The values of the derivative for each sensor channel together with additional information like r.h. or temperature were then used as input for the model. The plots below show the prediction as a certain class within the model. We tested the algorithm with other data from open- and smoldering fires as well as cigarette smoke (as nuisance). Figure 12 shows the prediction with respect to no fire, open (flaming) fire, smoldering fire and cigarette smoke. Some smoker events were misinterpreted as smoldering fires which of course is due to its nature.
Figure 12: Results of Model 1 (calculation performed by taking signals of 4 layers). The graphs show the prediction of the different events (flaming fire, smoldering fire and smoker) for flaming fires (top left), smoldering fires (top right) and smoking (bottom left). Higher prediction values mean better recognition. The red dotted line is the threshold above which the events are recognized.

The prediction algorithm could be implemented into a real time fire detection graphical user interface giving an according alarm after identifying fire and its classification. This setup was tested about 6 months later again with no remarkable change of prediction power.

5. Summary

Detecting fires alternatively with gas sensors or gas sensor arrays can improve the detection performance with respect to time to alarm and nuisance robustness. Most false alarms using photoelectric detectors are due to dust and water vapor and it can be expected that the investigated technologies at least do not respond to dust. A cross sensitivity on changes in humidity could be observed regarding to all sensor technologies but according cross sensitivities might be compensated by using an additional humidity sensor. The most important requirements for gas sensors to be used in fire gas detectors (point detectors)
are their long term stability, low price, low power requirements and limited cross sensitivities. PLSDA is an appropriate method for the recognition of fire and non-fire events for metals oxide sensors as well as for GasFETs. Metal oxide sensors show a strong cross sensitivity to ethanol and other solvent vapors, which implies that with respect to false alarm robustness signal processing is more challenging. Optodes may be a suitable technology but long-term stability has to be proven (bleaching). Due to the heat, smoke particles are mainly transported by convection with a minor contribution of diffusion whereas gas is transported by both convection and presumably with a higher fraction of diffusion. First results indicate that this is true at least for so called “heat layers” beneath ceilings [16]. These layers can occur during smoldering fires and are due to a temperature difference between near ceiling positions and the room. Aerosols are then not able to pass this layer for several minutes. Gas sensors used in this work responded some minutes earlier than conventional photoelectric detectors. Generally it can be stated that all of the presented technologies are able to reliably detect fires but one of the main issues is to suppress false alarms by identification of other situations which pretend fires. Accordingly, the used pattern recognition models and algorithms have to be tested extensively and have to be continually improved using field data – like this was also the case for photoelectric detectors in the past.

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