Articoli references notes

# A Miniaturised, Fully Integrated NDIR CO2 Sensor On-Chip

* CO2 long term exposure by humans can affect the organism: cognitive abilities, bones demineralization and kidney calcification
* Ventilation air quality dictated by sensors
* Also a low cost sensor can sometimes make the effect (electromechanical sensors and NDIR ones)
* ELECTROMECHANICAL SENSORS: measurement of gas concentration by measuring the change in electrical properties
  + Resistance
  + Capacitance
  + Electric potential

Induced by the absorption of a gas.

* ELECTROMECHANICAL SENSORS:
  + advantageous because of easy of fabrication
  + low cost
  + high sensitivity to wide range of compounds
* ELECTROMECHANICAL SENSORS: poor long-term stability and cross-sensitivity to other gases = less attractive in the CO2 sensor market
* NDIR CO2: superior long-term stability and high gas specificity: significant absorption strength of CO2 in mid-IR region.
* NDIR CO2: very high absorption coefficient of CO2 in mid-infrared: a path length of few centimeters is sufficient to detect small changes in CO2 concentration
* NDIR CO2: the 83% of the total advanced CO2 sensors are based on the NDIR technique
* NDIR CO2: are also bulky: long (several cm) interaction length is required for achieving ppm detection
* NDIR CO2: the cost is high because they are typically based on discrete co-assembled optical elements… in last years price and dimension changed giving them more interest in industry and academia
* NDIR CO2: decreasing the cost depending on the design of miniaturized ones, which can use a multi-pass cell or an optical cavity with various shapes.
* NDIR CO2: pre-concentrator coatings can be employed to effectively amplify the gas concentration in the vicinity of the optical field  the optical path length can be reduced
* NDIR CO2: broadband infrared source + reflective gas tube + 2 optical detectors that are sensing and reference … the overall mechanism allows for autocalibration
* NDIR CO2: mid-IR led has a relatively narrow emission spectrum such that the need for optical filters can be eliminated without introducing notable cross-sensitivity by other gases
* NDIR CO2: why integrating cylinder? Multiple reflections can be experienced by the sensor before reaching the detector and thus a long effective path length on a small sensor footprint
* NDIR CO2: the response time of the sensor usually depends on the level to measure in ambient (usually few hundreds of ppm), usually it could be long but there’s not a big problem for applications such as air quality monitoring
* NDIR sensor accuracy: can vary depending on the presence of water molecules (it depends on relative humidity RH in the air): the water vapor has a broad absorption in the infrared wavelength range that can be significant for some specific wavelength depending on the spectral overlap between the absorption band of the target gas and the water molecules
  + Different water interference characteristics
  + It is negligible in common ranges
* All sensors: characteristics curves used for determine some points of concentrations dependent on T and RH (that are made variable during the measurement)
* Stability of a sensor: deals with the degree to which the sensor’s characteristics remain constant over time. The drift can be attributed to factors such as temperature fluctuations and component aging.
* Sometimes it could happen that the reference signal and the sensing signal change in opposite directions during this drift (led photodiode characteristics): strong correlation between the ambient temperature and the sensing signal whilst the worse correlation of the reference channel is not yet fully understood

# Quartz-Enhanced Photoacoustic Spectroscopy: A Review

* Quantitative and qualitative gas sensors categorization: analytical sensors (gas-chromatography and spectrometry), electrochemical, semiconductor and laser optical absorption sensors  they are mainly classified based on the physical mechanism used
* Analytical techniques: no real time response, costly, invasive and with a large spatial footprint
* Electromechanical: relatively specific to individual gases, with usable resolution of less than one part per million of gas concentration and operate with a very small amount of current
  + Suited for portable, battery powered instruments
  + But there’s the influence of hysteresis and water humidity
  + Slow time response: fluctuations of gas and power up can make minutes for the sensor to reach 90% of tis final output value
* Laser absorption spectroscopy (LAS): response is < 1s and they are faster and part per quadrillion detection sensitivity (small traces detection)
  + Molecular absorption principle: transitions that an electromagnetic wave cause in a chemical species
  + If a molecule is irradiated by infrared light, it is excited to a rotational vibrational energy level manifold.
* Semiconductor lasers as light source for sensors: limited by the available optical power
* Mid-IR and previous analyzed NDIR are the common choice
  + Quantum cascade lasers (QCLs)
  + Interband cascade lasers (ICLs)

High output power

* LAS-based techniques: excellent sensitivity and selectivity and long effective optical pathlengths, compactness, mechanical stability, versability and cost effectiveness
* cavity ring down spectroscopy (CRDS): optical cavity with low loss and high reflectivity (>99.9%): long optical path of up to several kilometers. Multiple reflections occur on mirrors after a pulse
* Cavity enhanced absorption spectroscopy (CEAS): it is a modification of CRDS: radiation is injected at a very small angle respect to the cavity axes. It results in the formation of a dense structure of a weak optical axial modes that makes the system more robust against instability in both cavity and laser spectrum.
* Cavity output spectroscopy (ICOS): similar to CEAS: measurement procedure is the comparison between signal amplitude both at input and output of cavity.
* Photo-acoustic spectroscopy (PAS): one of the most robust and sensitive trace-gas optical detection techniques. Extremely high detection sensitivities with compact and relatively low cost absorption detection module (ADM)
* PAS: is based on optical absorption procedure as ICOS, CEAS and CRDS as well. It differs in the physical phenomenon used for the detection of the absorption signal.
* PAS: .when light at a specific wavelength is absorbed by the gas sample, excited molecules will subsequently relax to the ground state either through emission of photons or by the means of non-radiative process: it produces localized heating in the gas which in turn results in an increase of the local pressure. If incident light intensity is modulated, generation of thermal energy in the sample will also be periodic and a pressure wave (a sound wave) will be produced having the same frequency of the light modulation.
* PAS signal: can be amplified by tuning the modulation frequency to one of the acoustic resonances of the gas sample cell.
* PAS: in this strategy no optical detector is required and the resulting sound waves can be detected by a commercial hearing aid microphone.
* PAS: In the adopted logic of calculus, there’s a linear relationship between the sample concentration and the photo-acoustic signal.
* PAS: also the noise can affect measurements as well. This noise is assumed to be independent from the optical excitation.
* PAS: the same technology of lasers and optical parameters oscillators of the near-IR and QCLs in mid-IR have been successfully applied to PAS
* PAS and 3 main noise sources:
  + caused by the radiation that is incident upon the walls of the PAS absorption cell
  + non selective absorption of the gas cell window
  + external acoustic noise
* PAS and signal to noise ratio improvement (SNR): different designs for PAS cells have been proposed and implemented including a resonant cell with acoustic buffers, windowless and a differential cell
* PAS and differential cell: it includes 2 acoustic resonators equipped with microphones having same responsivity at the resonance frequency of the cell. Since the laser light excites only one of the 2 resonators, difference between the two signals removes noise components that are coherent in both resonators
* PAS and trace gas sensing applications: atmospheric chemistry, volcanic activity, agriculture, industrial processes, workplace surveillance and medical diagnostics.
* PAS and other substances than CO2: nitric oxide (NO) from vehicle exhaust emissions, medicine and drug diffusion rates in skin and to detect trace concentrations of disease biomarkers such as ethylene (C2H4), ethane (C2H6) and pentane (C5H12) which are emitted by UV-exposed skin. NH3 for monitoring respiratory emission from cockroaches as well as detection of intake prohibited substances by athletes
* PAS low cost detectors on market: smoke detectors, toxic monitoring gas and oil sensors for monitoring hydrocarbons in water.
* Quartz-enhanced photoacoustic spectroscopy (QEPAS): alternative approach to photo acoustic detection of trace gas utilizing a quartz tuning fork (QTF) as sharply acoustic transducer. It detects weak photo acoustic excitation and allowing the use of extremely small volumes
* QEPAS: restrictions imposed on the gas cell by the acoustic resonance conditions are removed.
* QEPAS: the quartz crystal is low-loss and low-cost piezoelectric material
* QEPAS: QTF is a quadrupole which provides good environmental noise immunity
* QEPAS: the excitation laser beam passes through the gap between the prongs without touching them
* QEPAS: if a rotational-vibrational state is excited, a collision-induced vibrational to translation (V-T) relaxation follows with a time constant that for a particular molecule is dependent on the presence of other molecules and intermolecular interactions. This process is more sensitive for this technology compared with the PAS one.
* QEPAS: wavelength of laser is varied by changing the driving current when the temperature of the laser is fixed. DFB QCL is the light source applied in this case, EC-QCL: is used when both temperature and current are fixed and the optical frequency can be scanned by applying a modulated voltage to a piezoelectric translator attached to the diffraction grating element of the EC-QCL.
* QEPAS: sometimes wavelength modulation (WM) is employed to improve the QEPAS SNR, minimizing external acoustic noise for a QEPAS based sensor system (those are the WM QEPAS)
* QEPAS (WM): the wm description is based on an intensity representation of an optical wave, so that only the absorption of the sample is considered and dispersion effects due to the sample can be neglected. Those results are obtained after various modulation steps.
* Amplitude Modulation (AM) QEPAS: introduced because the vibrational spectra of most molecules consisting of more than five atoms are so dense that infrared absorption spectra consist in 100-200 cm-1 broad bands and spectroscopic identification of these species requires laser excitation sources with a wide spectral coverage
* Amplitude Modulation (AM) QEPAS: on a laser radiation. This is operated at f0 by means of square wave amplitude current modulation and QEPAS signals are detected by a lock-in amplifier at the same f0 frequency.
* Amplitude Modulation (AM) QEPAS are not background free. Residual radiation absorbed inside the gas cell produce a sound at the TF resonant frequency thus generating a coherent background.
* Amplitude Modulation (AM) QEPAS: background subtraction can be applied because generally it is stable over several hours. This is done also by the mean of normalization of signal and background for every spectral point and in post processing.
* Various architectures have been designed and implemented for the QEPAS realization (OB On-Beam QEPAS and Off-Beam QEPAS, which are characterized respectively by a perpendicular and parallel laser tube with respect to the QTF plane probing the acoustic vibration excited in the gas contained inside the ADM)
* And the fiber coupled QCL-QEPAS:
* QEPAS ranges of application in conclusion: they are demonstrated to be effective and mature for numerous real-world applications:
  + environment monitoring (CO, CO2, CH4, H2CO, C2HF, C2HF5, N2O, NO2)
  + industrial emission measurements such as at combustion sites and gas pipelines (Hcl, CO2, CH4, CO, Nox, CH2O)
  + urban emission coming from automobile traffic (Nox, Sox)
  + rural emission such as a horticultural greenhouse and fruit storage (C2H6, C2H4, CH4, N2o)
  + control for manufacturing processes (SF6, Hcl)
  + detection of medically important molecules (NO, CO, NH3, C2H6, H2S)
  + toxic gases (CH2o, Hcl, HCN, N2H4 etc.)
  + planetary science (H2O, CH4, CO, CO2, N2H4, C2H2)
  + environmental monitoring
* QEPAS have been for instance installed in a mobile laboratory to perform atmospheric CH4 and N2O detection near 2 urban landfill sites located in Houston: they recorded concentration values in a very good agreement (<5% difference) with those measured by the Aerodyne Research Inc. “QCL mini monitor” multi-pass optical sensor having a CH4 detection sensitivity of 300 ppt and N2O detection sensitivity of 60ppt, both in 1 s which demostrates the precision, stability and applicability of the QEPAS sensing technique.