Terahertz Gas-Sensors: Gas-Phase Spectroscopy and Multivariate Analysis for Medical and Security Applications

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***Abstract*—This paper describes a spectroscopic system for gas sensing applications. It is based on SiGe transmitters (TXs) and receivers (RXs) operating at frequencies around 245 GHz and 500 GHz. 2f spectra of volatile organic compounds (VOCs) were obtained using wavelength modulation spectroscopy (WMS). Chemometrical analysis of the spectra is performed by applying several multivariate analysis (MVA) techniques.**

Keywords—gas sensor, mm-wave, THz, VOC, biomarker, TIC, SiGe, transmitter, receiver, multivariate analysis, PCA, PLS, SIMCA.

I. INTRODUCTION

The qualitative and quantitative analysis of gases and VOCs is of importance for security and medicine. Mm-wave/THz gas spectroscopy is a very suitable tool for sensitive and specific gas-sensing [1], because small molecules and larger hydrocarbons have strong absorption lines in this frequency range [2]. MVA is widely applied on large data sets in order to perform chemometrical analysis [3]. In spectroscopy this is attractive because with MVA it is possible to identify components and to predict the amount of a specific gas in a mixture of several gases..

A. Medicine

Several thousand VOCs are found in the human breath and several hundred are related to certain diseases [4]. With mm-wave/THz spectroscopy it is possible to detect a variety of VOCs simultaneously and to offer a non-invasive diagnostic method. Table I lists a few VOCs classified as medical breath biomarkers with strong absorption lines around 245 and 500 GHz and with integrated absorption coefficients higher than 10^{-23} cm.

B. Security

A spectroscopic gas sensor should be capable of detecting minute amounts of toxic industrial chemicals (TICs). Due to the wide availability and use of TICs, there is a significant risk regarding a terroristic attack with TICs or an accidental release [5]. In addition, these gases are harmful for life and environment according to the US Environmental Protection Agency (EPA) [6].

TABLE I.

Molecule	*# Lines 238-252 GHz*	*# Lines 491-498 GHz*	*Biomarker for*	*TIC*	*EPA*
2-Propanol	826[a]	n.a.	Breast cancer, lung cancer		
Acetaldehyde	150	109	Liver disease, lung cancer		x
Acrylonitrile	439	545	Smoker		x
Acetone	21	62	Lung cancer, diabetes		x
Carbonylsulfide	1	0	Liver disease	x	x
Formaldeyhyde	0	1	Breast cancer	x	x
Methanol	75	17	Nervous disorder		x

Gases and VOCs, known as biomarkers or TICs or have an entry on the EPA-list of harmful substances. The second and third row shows the number of absorption lines in the stated frequency range with an integrated absorption coefficient higher than 10^{-23}cm. a: all absorption lines.

II. ENABLING TECHNOLOGY

The implementation of integrated TX and RX in SiGe BiCMOS technology offers a path towards a compact and low-cost system for gas spectroscopy at mm-wave/THz frequencies.

A. 245 GHz Transmitter and Receiver

For the frequency range between 238 and 252 GHz TX and heterodyne RX chips were fabricated [7]. The first stage of the local oscillator (LO) of TX and RX consists of a 122 GHz voltage controlled oscillator (VCO), which is controlled by an external phase-locked loop (PLL) with a 1/64 frequency divider. The LO frequency is processed by a one-stage amplifier and coupled to a differential frequency doubler, which is connected to an on-chip antenna. The antenna is of double-dipole type and structure with localized backside etching (LBE) for an increased antenna gain of 7 dBi. The TX has an output power of 1 dBm at 245 GHz. It is shown in Fig. 1a (die area: 2.3x1.3 mm^2). The RX consists of an identical LO-chain, which is differentially coupled to a subharmonic Gilbert-cell mixer connected to the same type of antenna used for the TX. Fig. 1b shows the RX with a die area of 2.7x1.3 mm^2 [8]. Additionally a 1x4 TX-array was fabricated with an increased output power of 7 dBm at 245 GHz. Fig 1c shows the 245 GHz TX-array with its die area of 3.1x5.4 mm^2 [9].

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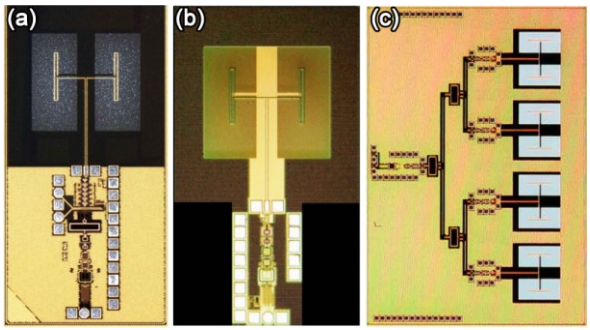

Figure 1: Photographs of (a) 245 GHz SiGe TX chip, (b) 245 GHz SiGe RX chip and (c) 245 GHz SiGe TX-array chip.

B. 500 GHz Transmitter-Array and Receiver

For the frequency range between 490 and 500 GHz a TX-array and a heterodyne RX-chip were fabricated. In contrast to the 245 GHz TX-array, the 1x4 TX-array includes frequency quadruplers instead of doublers and has an output power of -7 dBm at 500 GHz. The die area of the fabricated TX-array is 3.3x2.6 mm^2 and is shown in Fig. 2a [10]. The RX consists of a 122 GHz LO connected to a frequency doubler, and a transconductance subharmonic mixer connected to an integrated on-chip antenna. The die area of the fabricated RX-chip is 2.3x0.9 mm^2 (Fig. 2b) [11].

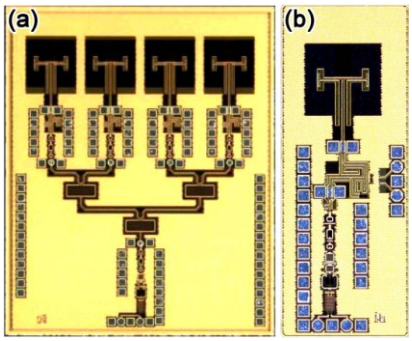

Figure 2: Photographs of a) left: 500 GHz SiGe TX-array chip, and b) right: 500 GHz SiGe RX chip

III. GAS SENSOR SYSTEM

A gas sensor system was developed using the 245 GHz and 500 GHz TX and RX chips.

A. 245 GHz Gas Sensor System

The spectroscopic system (Fig. 3) consists of an absorption cell with six deflection mirrors to obtain a beam path length of 1.9 m. The TX respectively the TX-array and the RX were bonded on plug-in boards, which were mounted on carrier boards with the external PLL. The TX respectively the TX-array was used as mm-wave/THz source. The divergent THz beam emitted by the antenna(s) was collimated by a plano-convex HDPE lens with a diameter of 40 mm and a focal length of 25 mm. The emitted beam is transmitted through the cell and certain frequencies are absorbed due to the gas inside the cell. Another plano-convex HPDE lens is focusing the radiation on the antenna of the RX chip. The gas pressure in the cell is controlled by a combination of a turbo-molecular pump, valves and a pressure gauge. The reference signals for both PLLs were delivered from two synthesizers (Rhode & Schwarz SMV01) with a mutual frequency offset of 24 kHz to obtain an intermediate frequency (IF) of 50 MHz. The synthesizer's frequency was swept by gradually stepping the reference frequency in intervals of $\Delta\nu = 244$ Hz corresponding to a spectral frequency resolution of $f_{res} = 0.5$ MHz as the multiplication factor is 2048 between the reference frequency and transmitter respectively receiver frequency. WMS was applied by modulating the TX's reference frequency. The modulation frequency f_M was set to 50 kHz with a frequency deviation D, which was adjusted in a way, that the modulation index β, which is the quotient of D and the full width half maximum (FWHM) of the absorption line, was approximately 2. The IF output signal of the RX was connected to a commercial Schottky diode (Agilent 8472B) and a subsequent lock-in amplifier (Stanford SR850). A digital input/output device (DAQpad) digitalized the analog output of the lock-in amplifier and a laptop recorded the 2f spectra. The setup is shown in Fig 3 and a photograph is shown in Fig 4.

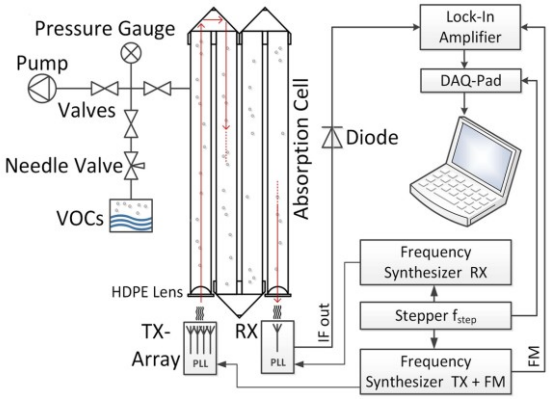

Figure 3: Scheme of the gas sensor setup.

Fig. 5 shows a 2f spectrum of 13 Pa methanol with the TX-array and a 1.9 m long absorption path, together with the integrated absorption coefficients taken from the JPL database for molecular spectroscopy [1]. The fingerprint-like spectrum demonstrates the excellent gas specificity. To extract the sensitivity of the gas sensor system, the signal to noise values (S/N) of 16 lines were determined. The signal S is calculated as the full peak height of the 2f-signal and the noise N is calculated as the peak-to-peak value in a 300 MHz free spectral bandwidth. The (S/N) values were plotted as a function of their corresponding integrated absorption coefficients at a pressure of 30 Pa and extrapolated to the value (S/N) = 1. The 245 GHz gas sensor system has a minimum detectable integrated absorption coefficient of 1.2×10^{-25} cm.

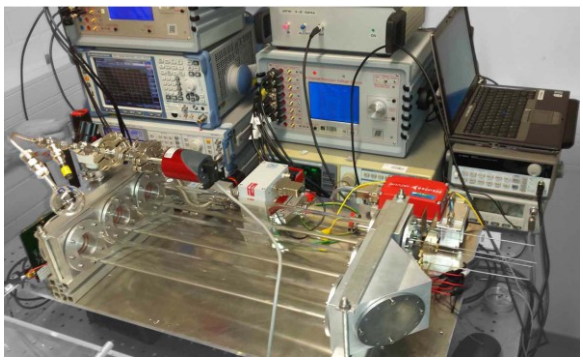
Figure 4: Photograph of the gas sensor setup.

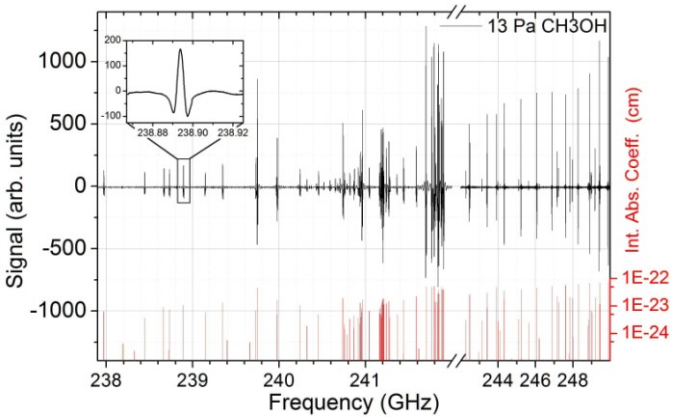

Figure 5: 2f spectrum of 13 Pa methanol.

B. 500 GHz Gas Sensor System

The spectroscopic system is similar to the 245 GHz sensor system, except for an additional band pass filter with a 75 MHz pass band and a low noise amplifier with a gain of 34 dB in front of the Schottky diode. The IF was set to 780 MHz and the spectral resolution was f_{res} =1 MHz. Fig 6 shows a 2f spectrum of 17 Pa methanol. The sensitivity in terms of the minimum detectable integrated absorption coefficient is 7.1×10^{-24} cm.

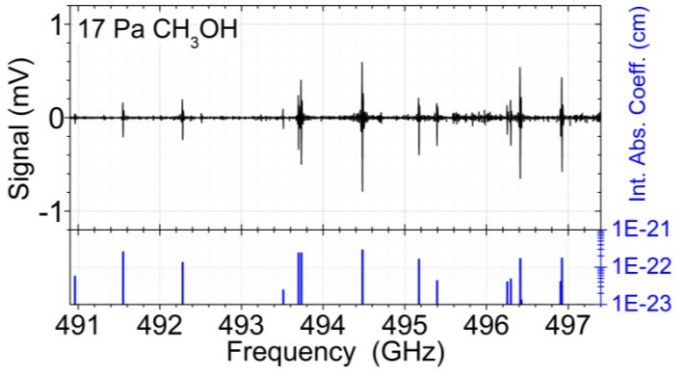

Figure 6: 2f spectrum of 17 Pa methanol.

IV. GAS CONCENTRATOR

In order to detect a gas, which is diluted in air under atmospheric conditions, the gas was concentrated. Fig. 7 shows the gas concentrator, which consists of a glass capillary with an inner diameter of 3 mm, filed with 200 mg Carboxen 1000 with a bed length of 19 mm, which is a carbon molecular sieve that acts as an adsorbent. Silicate glass wool keeps in place the adsorbent and a constantan wire is wrapped around the capillary, which acts as a heater for a thermal desorption of VOCs and/or gases adsorbed on the adsorbent surface. A heat resistant ceramic is used as a coating.

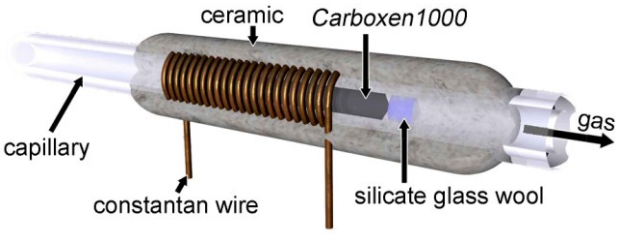

Figure 7: Scheme of the gas concentrator.

Fig. 8 shows 2f spectra of 100 ppm and 500 ppm methanol in 2.3 liter air, obtained with the 245 GHz and the 500 GHz gas sensor system with attached gas concentrator. For thermal desorption, the concentrator was heated to 290°C for both, an initial cleaning and the release of concentrated gas. The sensitivity is obtained by dividing the ppm-concentration by the (S/N) of the respective strongest line. The 245 GHz and 500 GHz gas sensor systems with concentrator have sensitivities of 3 ppm and 30 ppm.

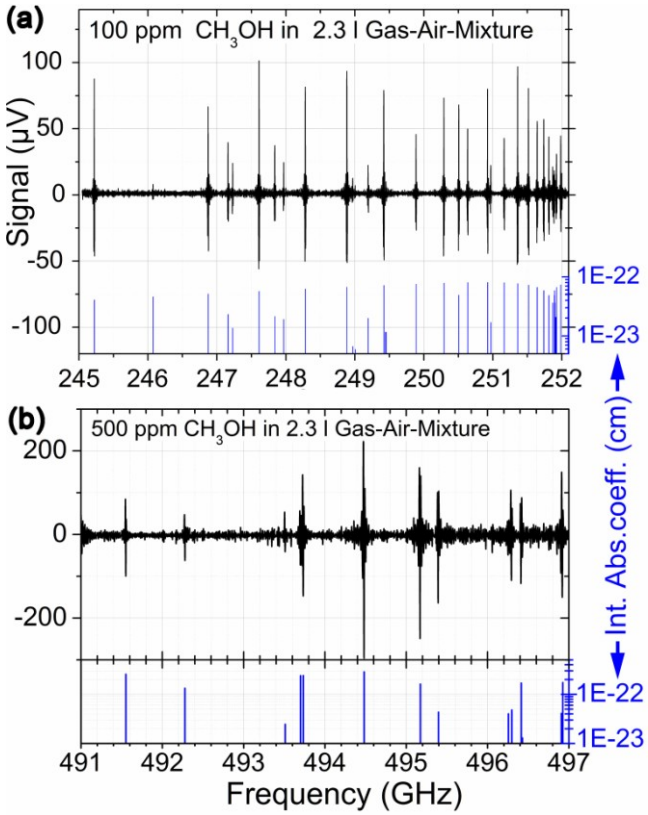

Figure 8: 2f spectrum of (a) 100 and (b) 500ppm methanol.

V. MULTIVARIATE ANALYSIS

We applied multivariate analysis (MVA) to the absorption spectra. For calculating a prediction model, we purposely selected seven VOCs known as biomarkers and/or are on the EPA-List (compare Table I) and prepared nine mixtures according to Table II with single shares down to 4 mol%.

TABLE II.

Molecule	*Symbol of sample (pure VOCs and VOC mixtures)*															
Acetaldehyde	x								x		x		x		
Methanol		x					x	x		x	x		x		x
Deut. Methanol[a]			x							x					
Acetone				x			x					x		x	
2-Propanol					x									x	
Acetonitrile						x			x		x				x
Ethanol							x		x			x	x	x	x

Selected VOCs. The crosses indicate the presence as a pure substance or in a mixture. a: Deuterated Methanol CH3OD.

Absorption spectra were obtained, using a vector network analyzer (VNA) with frequency extenders instead of TX and RX chips. We measured more than 1000 spectra of the 16 samples (VOCs and VOC mixtures) in the pressure range between 10 to 5000 Pa, with a spectral resolution of 500 kHz. Chemometrics was performed with MVA, in particular principal components analysis (PCA) and partial least squares (PLS) regression. These methods reduced the high dimensional spectra with its 28,000 data points to a few numbers (Scores). The Scores are forming clusters and even in two dimensions a clustering is found (Fig. 9).

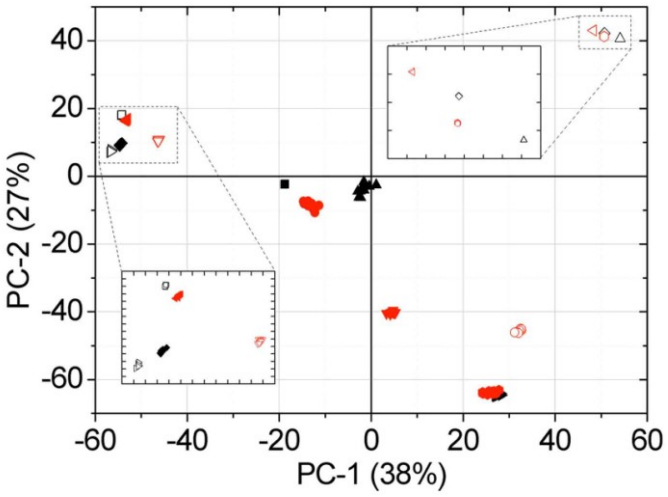

Figure 9: 2D Scores Plot. The spectra of the 16 samples at a pressure of 300 Pa are forming clusters.

A subsequent PLS constituted a qualitative and quantitative prediction model with a prediction accuracy of 2 mol% [12]. These models also offer a high flexibility, since a mm-wave/THz gas sensor becomes sensitive to different gases by simply updating the PLS prediction model. Additionally a soft independent modeling of class analogy (SIMCA) was calculated, which combines a number of single models to the most comprehensive prediction model. A subsequent quality analysis regarding additional noise showed good model robustness up to 2 % baseline noise and pressures up to 300 Pa. That implies a potential use of small and light-weight membrane pumps for vacuum generation, ensuring the compactness of a future sensor system.

VI. Conclusion

We showed the feasibility of a gas sensor, based on mm-wave/THz spectroscopy around 245 and 500 GHz. This sensor includes TX-, TX-array and RX-chips in SiGe BiCMOS technology. The unique fingerprint spectra of VOCs and TICs and the applied wavelength modulation technique makes the mm-wave/THz gas sensor very specific and sensitive with minimum detectable absorption coefficients as low as $1.2x10^{-25}$ cm. A carbon molecular sieve is used as a gas concentrator to increase the sensitivity of the sensor. An automatic spectral analysis can be performed with multivariate algorithms like PCA, PLS and SIMCA. The calculated prediction models showed a qualitative single share detection accuracy of 2 mol% in a VOC mixture. This approach offers a stable and flexible sensor application by simply updating the model. As the models are accurate for pressures higher than 300 Pa, small light-weight membrane pumps can be applied in future. This makes the mm-wave/THz spectroscopic gas sensor a promising tool for sensing applications in medicine and security.

Acknowledgment

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