SAWs for chemical sensing – optimizing receptor layers and transducers in respect to analytes of interest

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Introduction:

Mass-sensitive detection is the most universal strategy to combine chemically sensitive layers with transducer principles. Each adsorption or absorption of analytes both in gaseous or liquid phase will lead to mass changes resulting in resonance frequency deminishing of the device. High frequency resonators as the Quartz-Crystal-Microbalance (QCM) or the Surface-Acoustic-Wave (SAW) oscillator [1, 2, 3] show these frequency responses to analyte incorporation into the coatings. The Sauerbrey equation is valid for rigid materials, thus the answer will increase in parallel to the square of the resonance frequency. The resonance frequency can be enhanced up to approximately two GHz which lead to superior applications in comparison to QCMs. In Fig. 1 the sensor response of SAWs in the frequency range from 100 MHz to 400 MHz to identical mass load is shown, visualizing an approximately quadratic relationship. In parallel to frequency enhancement, however, the noise will increase. In spite of this fact the signal/noise ratio is linearly related to the resonance frequency resulting in an overall net effect in measuring conditions. SAW resonators include in addition to transducers reflector electrodes, guaranteeing to keep the electromagnetic energy within the device leading to low damping. Furthermore, the size of SAW resonators is drastically reduced going to e.g. 1 GHz. The length of a dual line is aspproximately only two mm. In this way optimised arrays can be designed for improving selectivity by pattern recognition procedures.

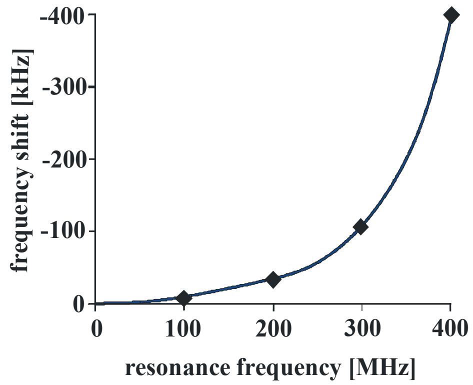

Fig. 1: SAW response to mass load as function of resonance frequency

SAW transducers:

Well known piezoelectrical materials are quartz, lithiumtantalate and lithiumniobate. Gas phase measurements can be performed with quartz devices in typical resonance frequencies ranging from 430 MHz to 1 GHz with Rayleigh-waves. In this case a low damping is observed leading to a mass-sensitivity below one p-gram. Electronic circuits are favourably designed using ring oscillators. In this way a constructive interference is obtained to generate stable oscillations. Furthermore, in dual arrangements interferences stemming from temperature or humidity fluctuations are compensated for. When liquid phase measurements are performed Rayleigh waves will lead to a high damping, however, thus no resonance is observed. This problem can be solved in going to shear waves (Fig. 2). Quartz shear devices will work in media of low dielectric constant, but going to water short circuit will be observed. In this case lithiumtantalate is a superior material since the surface waves are guided by the substrate due to its high dielectric constant. The substrate will cause, however, some broadening of the resonance peak in comparison to quartz (Fig. 2). Lithiumniobate is seldom used in chemical sensing, the change of one degree of temperature will

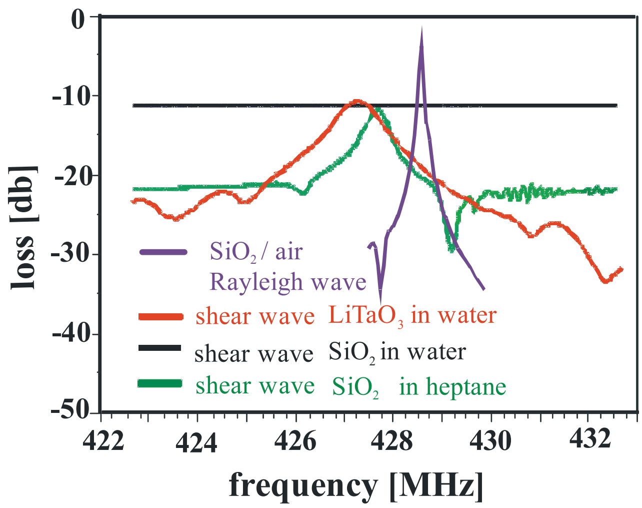

Fig. 2: SAWs in air and liquids

cause a frequency shift of many kHz, exceeding the chemical response. Here, differential measurements are often not successful to compensate for temperature fluctuations as in the case of other materials.

SAW receptor layers - applications:

The high sensitivity of SAW transducers makes possible the application of mono-layers as sensitive coatings. Thus, diffusion processes are eliminated and nearly instantaneous responses are obtained. The quartz surfaces of SAWs can be hydrophobized by silylchloride spacers converting their polarity. Thus, humidity cross sensitivities are eliminated, favouring the detection of all types of hydrocarbons. Otherwise, humidity would lead to hydrolysis of the -Si-O-Si- silyletherbonds and silanols are formed. In this way the mechanical properties of the quartz surface are changed and can lead to sluggish frequency responses. In this way even Antisauerbrey behaviour can occur. Silylspacers with an equal length, e.g. an octenyl chain will create hydrophobic interaction sites. In this way e.g. hydrocarbons are enriched on the SAW coating, leading to a dimished resonance frequency. Hydrophobic molecules can be detected down to a few ppm, selectivity is based on the molecular weight of the analytes. Furthermore, patterning the surface with silyl spacers in a different elongation will create molecular cavities for engulfing efficiently aromatic and halogenated hydrocarbons. This type of host-guest chemistry will distinguish between isomers, e.g. xylenes, which differ only in respect to their geometry. In this way not only chemical recognition by hydrophobic and hydrophilic interactions, but also by sterical properties via molecular hollows is performed. These ideas are further developed by linking molecular cavities such as cyclodextrines and calixarines to the SAW-surfaces. This can be performed by electrostatic strategies, improved stability is obtained, however, by covalent anchoring to the surface (Fig. 3).

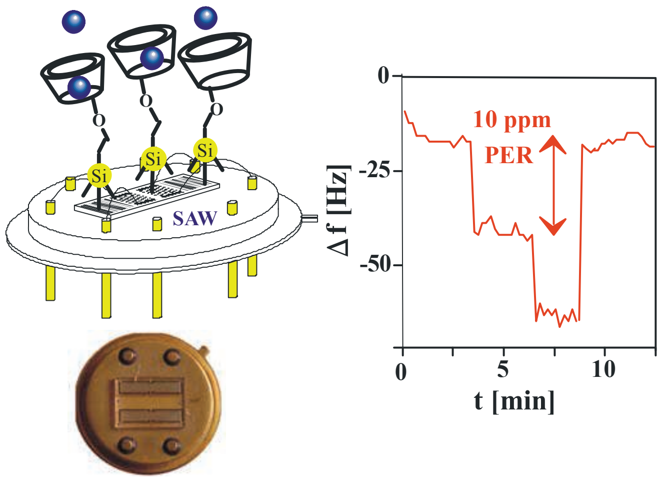

Fig. 3: Covalently linked molecular hollows, response to tetrachloroethylene (PER)

Supramolecular strategies according to host-guest chemistry can be combined with technological progress in sensor fabricating via molecular imprinting. For this purpose highly cross-linked prepolymers are applied by spin off processes to wafers. The analytes to be detected are added to the monomer mixtures as templates. After polymerisation the templates are removed. In this way suitable cavities are generated for re-incorporation of analytes. Typical layers heights of the sensitive coatings on the piezoelectrical substrates are some nano-meter to guarantee adequate response times (Fig. 4). Thus, the production of the transducer is combined with the sensitive layer. Additionally, not only distinct analytes can be detected, but complex mixtures are characterized, too. Monitoring of composting processes, automotive oil degradation [4] and food quality is performed by these synthetic antibodies.

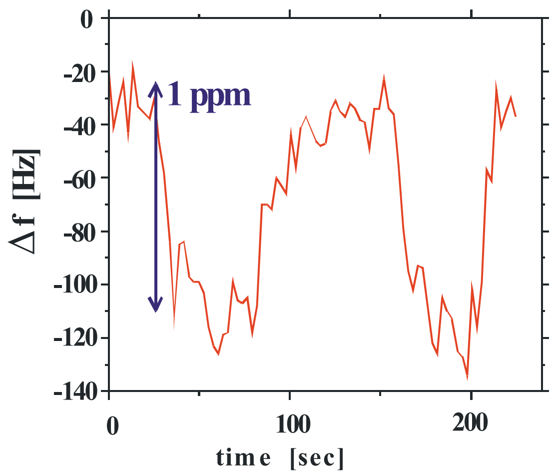

Fig. 4: 1 GHz SAW sensor response to m-xylene

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